APPLIED Spectroscopy

SOCIETY for APPLIED SPECTROSCOPY

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1961

Vol. 15 No. 5

PUBLISHED BY THE SOCIETY FOR APPLIED SPECTROSCOPY

APPLIED SPECTROSCOPY is a bimonthly publication of the *Society for Applied Spectroscopy*. Formerly called the BULLETIN OF THE SOCIETY FOR APPLIED SPECTROSCOPY, the volume numbers are a continuation of those of the BULLETIN.

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Esso Research & Engineering Co.
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October Issue—Published Bimonthly—
Vol. 15, No. 5, 1961

Second Class Postage
Paid at Plainfield, N. J.

Known office of publication: P.O. Box 1228, 417 Cleveland Avenue, Plainfield, New Jersey

POSTMASTER: Send form 3579 to the publication office.

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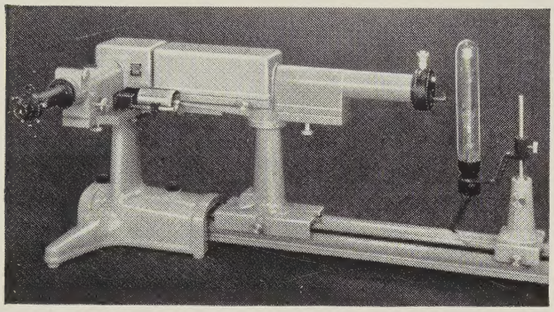

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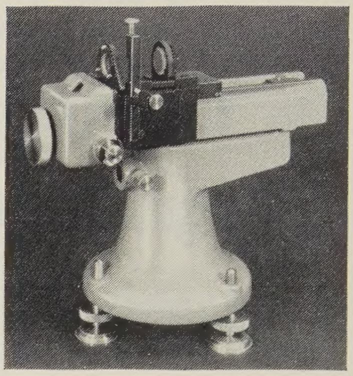

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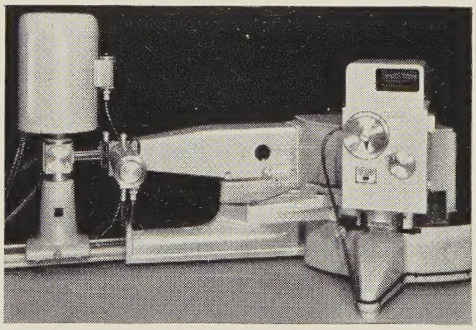

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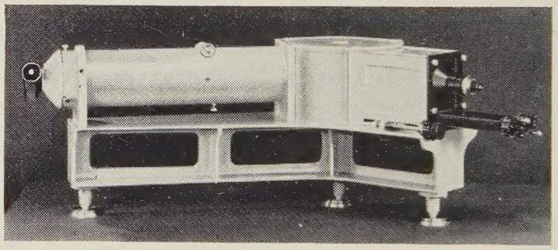

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HILGER & WATTS

What's New?

Editor—Rodger W. Loofbourow

[Contributions for this column should be sent to its Editor, Mr. Rodger W. Loofbourow, Crobaugh Laboratories, 3800 Perkins Avenue, Cleveland 14, Ohio.]

The name of Scope, Inc. has been changed to Research and Control Instruments, Inc., according to an announcement by Jason L. Saunderson, President.

RCI is planning new instruments in the fields of *direct reading spectrometry and chromatography*. It is expected that they will begin to make deliveries this fall. The RCI office and plant are located at 10 Jefferson Avenue, Woburn, Mass.

——— λ ———

The Electronic Calibration Center of the National Bureau of Standards Radio Standards Laboratory, Boulder, Colorado has recently initiated a service for the *calibration of waveguide reflectors* in the microwave frequency region. The service is presently offered in WR-90 waveguide size throughout the frequency range 8.2-12.4 Gc. Calibrations of high accuracy are obtained through the use of a modified reflectometer system. The waveguide reflectors are calibrated by comparison with an NBS-designed working standard employing a straightforward method that can be adapted for use in other standards laboratories.

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The National Bureau of Standards has discontinued the certification of emf of unsaturated standard cells as of June 30, 1961. An exception will be made for public utilities and other agencies having operations of such a nature as to require these services from the Bureau. This action is in keping with the Bureau's long-standing policy of discontinuing certain measurement services, which become adequately available at other laboratories. The Bureau will continue, however, to conduct referee tests or to undertake calibration of unsaturated cells when special or unusual circumstances are involved.

——— λ ———

A contract to develop and build a *rocket-borne spectrometer* to study ultraviolet energy emitted by stars has been awarded to the Perkin-Elmer Corporation by the Princeton University Observatory.

The special instrument will be carried above the earth's atmosphere in an Aerobee-Hi rocket to measure the U.V. emission of a brilliant star. The observation will be recorded at a height of 62 to 143 miles above the earth during a period of less than five min and will be telemetered back to earth.

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The American Society for Testing Materials announces the availability of a 62 page list of publications including Symposia, Manuals, Special Publications, Indexes, Compilation of Standards, Charts, Reference Photographs, and Reports. More than 300 items are fully described and forty of them are new. This list may be obtained without charge by writing to the American Society for Testing Materials, 1916 Race St., Philadelphia 3, Pennsylvania.

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A new *glass for calibrating spectrophotometers* is available from the Optical Sales Department, Corning Glass Works, Corning, New York.

The filter, No. CS 3-138, has several sharp absorption bands well spaced throughout the ultraviolet and visible regions of the spectra, 241 to 2000 mμ. Prominent bands are located near 241, 280, 288, and 360 mμ.

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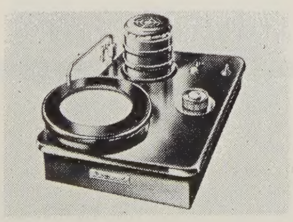
A new *polisher-grinder*, UNI-POL, is now available for fine metallographic specimen preparation. It is manufactured by Geoscience Instrument Corporation, 142 Maiden Lane, New York 38, N. Y.

The UNI-POL is a versatile machine which incorporates an 80-1200 rpm variable speed control with a powerful semiconductor ½ hp dc motor providing constant torque at all loads. The pan, lap, polishing wheel, and cover can be changed as one unit in seconds without dangers of contamination.



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A three-color *pyrometer*, capable of making 1000 temperature determinations every second, has been developed by the National Bureau of Standards.

This instrument forms a spectrum of the radiation from the source, masks out all but the three required wavelengths, and presents these wavelengths to the detector sequentially. When operating at high speed it is necessary to record the data, with an oscilloscope, magnetic tape, or other high speed recorder. The three-color instrument eliminates certain limitations in one and two color pyrometers and can give temperature readings in the 1000 to 3000°C range with an uncertainty of about 1%. The criterion which must be met to insure this accuracy is that the emissivities are a linear function of the wavelengths selected. Potential applications include the measurement of the temperature of missile components during firing tests, of ablating nose-cone materials and of exploding wires.

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A new *direct reading spectrometer* has been announced as the first product offering of Research and Control Instruments, Inc., Woburn, Massachusetts.

This instrument offers three independent optical systems which may be used individually or in any combination. One sample excitation emits light to any or all of the systems. The optical systems include (1) an Air Spectrometer, (2) a Vacuum Spectrometer, and (3) an Auxiliary Spectrograph.

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A new *X-ray analyzer crystal* has been developed by the Isomet Corporation, Palisades Park, New Jersey. This crystal has a 2-d spacing of 26A and extends the range of X-ray spectrometers by permitting the analysis of the lighter elements.

Isomet also offers Laser crystals in boule form or fabricated rod with ends polished optically flat and parallel. The reflective surfaces are evaporated metallic coatings or multiple dielectric layers. Stock crystals include ruby and CaF_2 doped with divalent samarium or trivalent uranium. Custom grown crystals such as CaF_2, CdF_2, BaF_2, and MgF_2 can be obtained with activators such as the rare earths or the transition elements.

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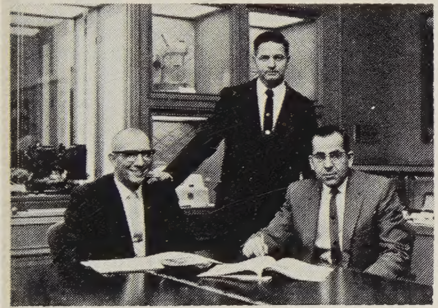
The Spectral Line

Editor—S. Richard Wiley

[News about members and matters of interest to spectroscopists may be sent to the Editor, S. R. Wiley, 1239 Owen Brown Rd., Ellicott City, Md.]

Three new departments have been established to provide greater specialization within Bausch & Lomb's extensive line of laboratory and industrial instrument products. The departments, to be headed by personnel promoted from within the sales staff, include: Industrial Sales Department, *Robert L. Grau;* Laboratory Sales Department, *David J. Joerger;* and Analytical and Photogrammetric Sales Department, *James F. Starks.* Each will report to Herbert J. Mossien, Sales Manager, Instrument Division.

Mr. Grau, a graduate of the University of Rochester, joined B & L in 1956. Mr. Joerger, with B & L since 1949, was graduated from Alfred University, and Mr. Starks, Syracuse University graduate, has been with the Company since 1950.



Left to right: David J. Joerger, Laboratory Sales; James F. Starks, Analytical and Photogrammetric Sales; and Robert L. Grau, Industrial Sales.

—— λ ——

William Driscoll has been appointed sales engineer for infrared-spectrochemical instruments for Baird-Atomic, Inc. Mr. Driscoll in his new position will be responsible for the sale of the firm's infrared-spectrochemical instruments in Ohio, West Virginia, North Dakota, South Dakota, Illinois, Iowa, Minnesota, Nebraska, Wisconsin, Indiana, Kentucky, Michigan, and Manitoba and Western Ontario, Canada, with sales headquarters located at 540 North Lake Shore Drive, Chicago, Illinois. Prior to his joining Baird-Atomic, Inc., Mr. Driscoll was as-

(Continued on page 11A)

Spectral Line—

(*Continued from page 9A*)

sociated with Nuclear-Chicago Corporation and previously had been engaged in research activities with the Argonne National Laboratory.

Mr. Driscoll received his B.S. and M.S. degrees in Chemistry from Loyola University of Chicago. He resides with his wife and one son in Elmhurst, Illinois.

——— λ ———

Nathaniel Brenner has been appointed Product Line Manager for Laboratory Gas Chromatography at the Perkin-Elmer Corporation. He has previously served as applications engineer and laboratory supervisor in the Instrument Division. In 1957, he was appointed a Product Specialist and became Manager of Applications Engineering in 1959. Prior to joining Perkin-Elmer, Mr. Brenner was a spectroscopist with the Aero Materials Laboratory of the U. S. Navy. He received a B.S. in Chemistry from Queen's College, N. Y.

——— λ ———

Dr. Heinrich B. Kessler has been appointed Product Line Manager for Laboratory Infrared at the Perkin-Elmer Corporation. Dr. Kessler joined the company as Manager of Infrared Planning for the Instrument Division in July 1960. Prior to joining Perkin-Elmer he was a sales technologist with E. I. duPont de Nemours & Co. He received his A.B., M.S., and Ph.D. degrees in Physics from the University of Michigan.

——— λ ———

Dr. C. L. Grant has joined the faculty of the University of New Hampshire as Research Associate Professor in the Engineering Experiment Station. For the past several years, he was in charge of the Analytical Spectroscopy Laboratory for the New Jersey Agricultural Experiment Station at Rutgers University. He will conduct similar activities at his new location.

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APPLIED SPECTROSCOPY

Published by the Society for Applied Spectroscopy

Volume 15 No. 5, 1961

X-Ray Spectrographic Determination of Thorium in Low Concentrations

J. N. van Niekerk†, F. W. E. Strelow*, and F. T. Wybenga

National Physical Research Laboratory, Council for Scientific and Industrial Research, Pretoria, South Africa

Abstract

A method is described for the rapid determination of small concentrations of thorium. The thorium is first concentrated on a suitable cation exchange resin and then measured directly on an x-ray spectrograph. With the experimental conditions employed it is shown that the extraction of thorium is practically quantitative. Both column and batch extraction methods were investigated, and it is shown that the latter technique is superior both as regards reproducibility and time of analysis. It is further shown how interference effects due to co-adsorbed elements, such as iron, can be overcome by the use of a suitable internal standard. From calibration curves so obtained the thorium concentration in three unknown samples was determined, and the results are compared with those obtained by chemical analysis.

Introduction

In two previous communications *(3, 4)* it has been shown how a combination of ion exchange and x-ray fluorescence techniques has extended the scope of x-ray spectrography to make possible the analysis of trace concentrations of uranium, while maintaining such desirable features as speed of analysis, accuracy, etc. In this paper it is shown how this technique has been applied to determine small amounts of thorium, an element which, in trace quantities, very often requires time consuming separation procedures such as liquid-liquid extraction, co-precipitation, or ion-exchange chromatography before it can be determined by conventional methods.

The method should be useful for the routine analysis of low grade thorium ores or for the determination of thorium in higher grade ores by using conveniently dilute solutions.

Extraction of Thorium with Solid Resins

Anion Exchange Resin

Since uranium and thorium both form sulphate complexes and as previous work *(4)* had shown that the anion exchange resin AG-IX, in sulphate form, has a high affinity for uranium, it was decided to try this resin first as a possible extractant for thorium. On using 2.5 g of dry resin, a determination of the equilibrium distribution coefficients (K_d) in acidified 0.25*M* $(NH_4)_2SO_4$ (pH 2.5-3.0) gave values as shown in Table I. From these results it is obvious that AG-IX is not a suitable resin for the extraction of thorium.

TABLE I. DETERMINATION OF K_d FOR VARIOUS CONDITIONS

Total Amount Present in Exchange System	*Resin*	*Medium*	K_d
0.1919 g U_3O_8	AG 1X10	0.5 *N* $(NH_4)_2SO_4$,pH 2	1739
0.0480 g U_3O_8	"	"	4350
0.2814 g ThO_2	"	"	30.2
0.0711 g ThO_2	"	"	46.9
0.3501 g ThO_2	AG 50WX8	0.5 *N* HCl	$>10^5$
"	"	1.0 *N* HCl	2049
"	"	2.0 *N* HCl	239
0.0875 g ThO_2	"	0.5 *N* HCl	$>10^5$
"	"	1.0 *N* HCl	17420
"	"	2.0 *N* HCl	922

Cation Exchange Resin

To obtain more effective extraction, a resin with a higher K_d for thorium was necessary. Strelow *(1, 2)* has shown that the cation exchange resins, AG 50WX8 and AG 50WX12, in hydrogen form, have a high affinity for thorium and can be used for the chromatographic separation of thorium from a large number of other elements. AG 50 resins are sulphonated polystyrene cation exchange resins supplied by the BIO - RAD Laboratories of Berkeley, California and can be obtained in a variety of cross-linkings and particle sizes. The K_d values for AG 50WX8** using 2.5 g resin (12.5 meq./g capacity) were determined and are given in Table I. From the results it follows that with these resins the extraction of thorium should be much improved. It was therefore decided to carry out both batch and column extraction experiments with AG 50WX12 resin and to determine the adsorbed thorium directly with an x-ray spectrograph.

Experimental

Batch Extraction

For all the batch extraction experiments 2 g of AG 50WX12 resin (dry wt) were shaken in a Gallenkamp mechanical shaker together with 500 ml of 0.5*N* HCl

†Present address: Research Department, S.A. Iron and Steel Corporation, Pretoria

*National Chemical Research Laboratory

**The K_d values for AG 50WX12 resin are still higher than those for AG 50WX8.

containing known amounts of thorium. Unless specified otherwise this acid concentration was used throughout. The resin was separated by filtering through a sintered glass crucible (No. 1 porosity) and washed over into a suitable sample holder *(5)* with 5 ml distilled water. After allowing the resin particles to settle for about one min, the net Th $L\alpha_1$ peak was measured (using one min counting times) on a Philips PW1010 x-ray spectrograph, fitted with a high intensity Mo tube, a LiF crystal, and a scintillation counter.

To investigate the effect of shaking times on thorium extraction, a solution containing 1 ppm ThO_2 was used. The mean Th $L\alpha_1$ intensities of triplicate extractions were measured and plotted (Figure 1). The cross on this diagram represents the intensity obtained when shaking for 1 hr. From the general form of this curve and the close agreement (within experimental error) of the intensities recorded for 10 and 60 min shaking times, it can be inferred that the extraction of thorium under these conditions is very nearly quantitative.

The practically quantitative extraction of thorium was further demonstrated by carrying out three batch extractions with solutions containing $495 \pm 3 \mu g$ ThO_2. Ten min shaking times were used, and the resins and solutions were subsequently analysed by chemical methods. In every case less than $2 \mu g$ ThO_2 remained in the solution, showing that under the chosen conditions the extraction is better than 99.5%. In all subsequent batch extraction experiments a shaking time of ten min was used.

Although the equilibrium distribution coefficients of thorium for AG 50 resins in HCl solutions have been determined by Strelow *(1)*, it was felt that the influence

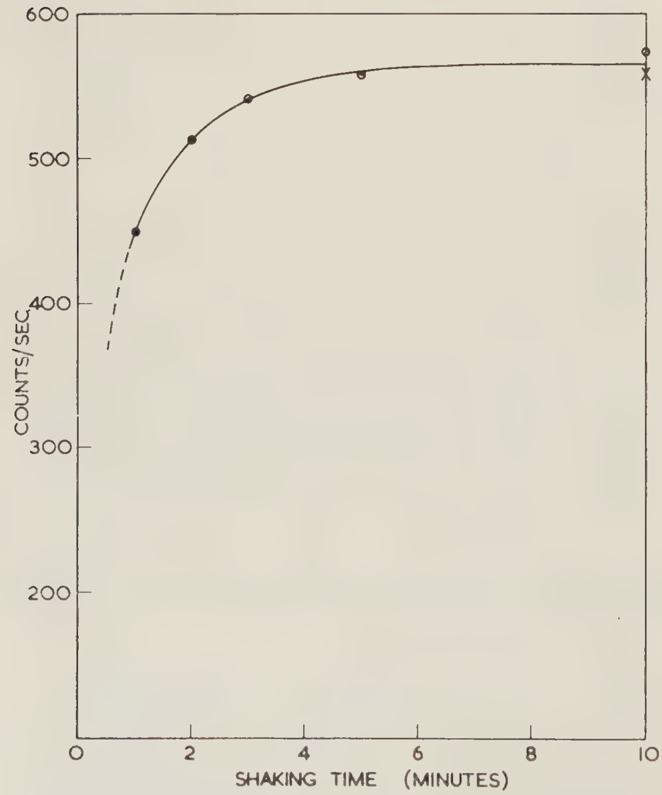

FIG. 1. EFFECT OF SHAKING TIME ON THORIUM EXTRACTION

0.5 mg ThO_2 in 500 ml 0.5 *N* HCl shaken with 2 g AG 50WX12 resin for different periods.

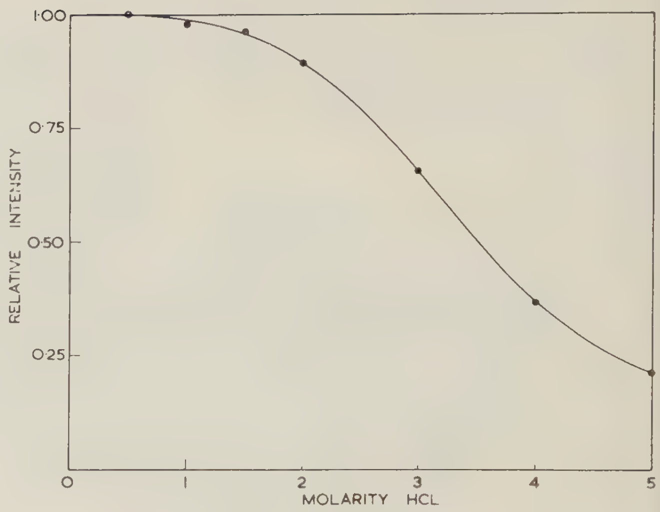

FIG. 2. INFLUENCE OF HCl CONCENTRATION ON THORIUM EXTRACTION

0.5 mg ThO_2 in 500 ml solution of varying HCl concentration shaken with 2 g AG 50WX12 resin for 10 min.

of HCl concentration on the amount of thorium extracted under the present experimental conditions should be investigated. Using 500 ml of a solution containing 1 ppm ThO_2 and different HCl concentrations, triplicate extractions were made and the net Th $L\alpha_1$ peak was measured for the various acid concentrations. The results, which are plotted in Figure 2, are in general agreement with those obtained by Strelow when it is kept in mind that, for example in 4*N* HCl, only 61% of the equilibrium amount of the thorium is adsorbed on the resin in the first 10 min. These results again confirm previous conclusions that on using 0.5 *N* HCl solutions the extraction of thorium under these conditions is close to 100%. It should be pointed out that even with thorium concentrations as high as 40% of the total resin capacity present in the solution, the K_d value of thorium in 0.5 *N* HCl is still about 10^5 *(2)* and thus high enough to make the extraction of the thorium practically quantitative.

Apart from operational errors, such as weighing, measuring, setting, etc. and instrumental instability, there are three main sources of error in the method used here; these are statistical counting errors, which can be readily computed *(6)*, errors due to the non-uniform distribution of resin particles in the sample holder and thirdly, errors due to the lack of reproducibility in the extraction and resin recovery technique. To evaluate these errors, batch extractions were carried out on a 1 ppm ThO_2 solution. The standard deviations obtained for stationary and redistributed samples, as well as those from ten different extractions are shown in Table II. From these values it is

TABLE II. MAIN SOURCES OF ERROR IN THORIUM DETERMINATION[a]

Conditions	*Coefficient of Variation*		*Number of Samples*
Batch extraction, sample stationary	2.0	(1.61)[b]	10
Batch extraction, sample redistributed	2.2		10
Batch extraction, different extractions	2.8		10
Column extraction, different extractions	8.1		9

[a] 1 ppm ThO_2 solution
[b] Computed statistical counting error

Table III. Linearity of Thorium Count with Concentration

Thorium added, ppm	Net Th $L\alpha_1$ peak height, c/s	Increment, c/s
1	554	554
2	1104	550
3	1663	559
4	2219	556
5	2807	588

evident that with this method of extraction good reproducibility can be achieved.

The feasibility of using this technique to establish calibration curves for the determination of thorium in solution is demonstrated by the results given in Table III. Here the increments in the net Th $L\alpha_1$ peak intensity, after extraction of thorium from solution, are given. In all the above investigations the peak to background ratio for 1 ppm ThO_2 solutions was about 1.6.

Column Extraction

When viewed in the light of quantitative separation, extraction of an element by means of chromatographic ion exchange columns offers distinct advantages over the batch extraction process, as for example in certain problems where it might be necessary to separate various elements on a quantitative basis. The feasibility of applying the present method on resin from a chromatographic column separation was therefore also investigated. Apart from the fact that these investigations were much more time consuming than the batch extraction experiments, the results obtained (Table II) were also inferior. The relatively high coefficient of variation should probably be accounted for by the fact that, because of the high K_d value, the top resin layers in the column will be primarily responsible for thorium adsorption. This will not only lead to additional distributional variations, but also to transfer errors should some of the thorium-rich resin grains get lost during transfer of the resin from the column to the sample holder.

Because of its greater reproducibilty and speed of analysis, the batch extraction technique was used in all subsequent investigations.

Interference by Iron

The elimination of interelement effects, resulting from the co-extraction of foreign elements together with thorium, was achieved by using a suitable internal standard in a manner similar to that previously described *(3, 4)*. In these studies increasing amounts of a standard $FeCl_3$ solution were added to 500 ml quantities of an one ppm ThO_2 solution and these batches were then treated with 2 g AG 50WX12 resin in the manner already described. After extraction, 5 ml of a standard KBr solution (0.5 g/l) were added to the resin, and after mixing thoroughly and allowing the resin particles to settle in the sample holder for about one min, the net Th $L\alpha_1$, Br $K\alpha$ and Fe $K\alpha$ peaks were counted.

Table IV. Use of Internal Standard to Overcome Influence of Co-Adsorbed Iron[a]

Amount Fe added, mg	$FeK\alpha$ c/s	$ThL\alpha_1$ c/s	$BrK\alpha$ c/s	$ThL\alpha_1/BrK\alpha$
0	0	640	1885	0.34
18.6	943	616	1811	0.34
37.2	1873	605	1634	0.37
55.9	3599	574	1678	0.34
74.5	4075	558	1587	0.35
93.1	4826	571	1639	0.35
130.3	6084	563	1616	0.35
186.1	7304	518	1427	0.36

[a] $FeCl_3$ added to 1 ppm ThO_2 solution

Table V. Application of Potassium Bromide As Internal Standard for the Determination of Thorium

ThO_2 added, ppm	Ratio, $ThL\alpha_1/BrK\alpha$	Increment[a]
0	0.00	
		0.40
1	0.40	
		0.38
2	0.78	
		0.37
3	1.15	
		0.38
4	1.53	
		0.40
5	1.93	

[a] Increase in the $ThL\alpha_1/BrK\alpha$ intensity ratio for the addition of 1 ppm ThO_2.

The suppression of the net thorium peak intensity by increasing concentrations of iron as well as the constancy of the Th $L\alpha_1$/Br $K\alpha$ intensity ratio (standard deviation about 3%) are shown in Table IV. These results fully substantiate the use of an internal standard when introduced in this manner.

The feasibility of also establishing calibration curves in terms of a suitable internal standard is shown in Table V. Here solutions containing 1 - 5 ppm ThO_2 were used, and after extraction the resin was mixed in the sample holder together with 5 ml of the standard potassium bromide solution and the Th $L\alpha_1$/Br $K\alpha$ intensity ratios were determined. In a similar manner the influence of other coadsorbed cations can be eliminated.

Analysis of Actual Samples

Three thorium bearing ore samples were prepared for x-ray fluorescent analysis in the following manner: 0.5 g samples were boiled for 90 min in 20 ml 70% $HClO_4$. After filtering, the filtrates were diluted to about 500 ml with distilled water, whence the final acid concentration of the samples was about 0.5 *N*. After extracting in the usual manner, the resin was mixed with 5 ml of the standard KBr solution and the Th $L\alpha_1$/Br $K\alpha$ ratio measured. Thorium concentrations were then determined from the calibration curve described in the previous section.

Table VI. Determination of Thorium in Ore Samples, % ThO_2

Sample	Chemical	X-ray
Q 390	0.583	
	0.584	0.59, 0.59
	0.580	
	Mean 0.582	
Z 409	0.227	
	0.225	0.22, 0.22
	0.222	
	Mean 0.225	
T 568	0.408	
	0.406	0.42, 0.43
	0.407	
	Mean 0.407	

The results of duplicate analyses of these samples are shown in Table VI, and these may be compared with the chemically determined values which are also given. The agreement is good and the accuracy is about that which is predicted by experiment ($\pm$ 3%).

Conclusion

The method described in this paper combines the virtues of both ion exchange and x-ray fluorescence techniques. The total time needed for an analysis, after the sample has been brought into solution, is about 20 min. The accuracy obtainable, when analysing for thorium in the ppm range, using 500 ml solutions, is about 3%. The sensitivity of the method under present experimental conditions is estimated to be 50 μg ThO_2 on 2 g of resin (std. dev. of 13%). Thus, when using 2 g of resin with 500 ml solution, it is possible to measure 0.1 ppm ThO_2 with the above accuracy.

The method seems to be ideally suited for the determination of thorium in low grade ores and for plant control analyses, while modifications of the technique should also find useful application in many other fields involving ion exchange separation.

Literature Cited

(1) F. W. E. Strelow, ANAL CHEM. **31**, 1201 (1959)
(2) F. W. E. Strelow, IBID. **32**, 1185 (1960)
(3) J. N. van Niekerk and J. F. de Wet, NATURE **186**, 380 (1960)
(4) J. N. van Niekerk, J. F. de Wet, and F. T. Wybenga, ANAL CHEM. **33**, 213 (1961)
(5) J. N. van Niekerk and F. T. Wybenga, APPLIED SPECTROSCOPY **14**, 56 (1960)
(6) P. D. Zemany, H. G. Pfeiffer, and H. A. Liebhafsky, ANAL. CHEM. **31**, 1776 (1959)

Submitted November 9, 1960

Some Characteristics of an Ebert Spectrograph*

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Abstract

Some of the characteristics of an Ebert 3.4 m plane grating spectrograph have been examined in order to ascertain the optimum conditions for its use in quantitative spectrographic analysis. Of special interest were the higher orders not conveniently reached by many spectrographs produced for general analytical work. A limitation on the use of high dispersions when the dc arc or ac spark is employed as the excitation source is discussed.

Introduction

The Ebert spectrograph, first described in 1889 *(1)*, has not been widely used by spectroscopists. Recently, however, following its independent rediscovery by Fastie *(2)*, there has been a renewed interest in this mounting which has resulted in the design of a monochromator *(2)*, a spectrophotometer *(3)* and a spectrograph *(4)* based on the Ebert principle. The spectrograph has been well described generally by Jarrell *(4)*, but we have found it advantageous to examine closely several of the instrument's characteristics in order to ensure that optimum performance is obtained for any particular analytical problem. The results of this study are given in the following pages.

Apparatus

The spectrograph, a Mark II model, was obtained from the Jarrell-Ash Company, Newtonville, Mass. (An optical diagram of the instrument is shown in Figure 1.) It was equipped with a nominal 6-in., 15,000 lines/in. plane reflectance grating and a bilateral variable slit. The grating was blazed to diffract the majority of the light intensity into the first and second orders of the visible and ultraviolet regions and was masked so that its effective width was 4.25 in. The focal length of the 16-in. diam. collimating mirror was 3.4 m. A 300-mm focal length lens was mounted at the slit to ensure uniform illumination of the slit.

A Jarrell-Ash "order sorter" *(4)* was used in conjunction with the spectrograph when work was done in orders higher than the first. The "order sorter" is essentially a low dispersion spectroscope which projects a vertical spectrum of the source on the slit of the Ebert spectrograph. Light of wavelength λ falls on a specific portion of the slit while light of another wavelength, for example 2λ, falls on a different portion. Since the Ebert mount is essentially stigmatic, these two wavelengths produce images on the photographic plate at different levels, corresponding to their position on the slit. In this manner the spectrum is "sorted" and overlapping orders avoided. The height of the spectral lines is determined by the height of the "order sorter" slit. For first order work the prism of the "order sorter" was slipped out of the light path, transforming the device into an effective three lens condensing system.

Intensity measurements were made using a low pressure cadmium vapour lamp as the source. Kodak S.A. No. 2

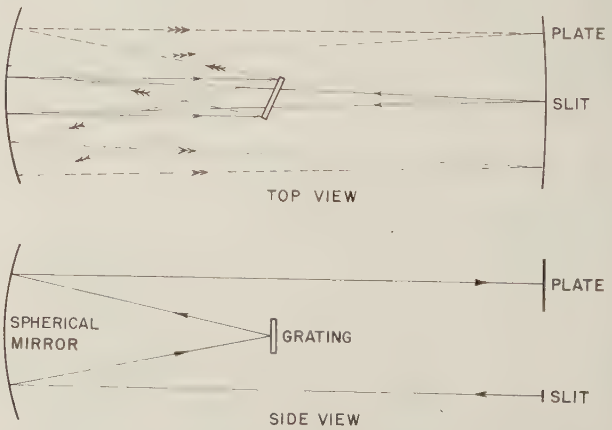


FIG. 1. OPTICAL DIAGRAM OF THE JARRELL-ASH EBERT SPECTROGRAPH

*Issued as N.R.C. No. 6500

ABLE I. A Typical Set of Dispersions Available At 4000 A

Order	i(Degrees)	Dispersion (A/mm)	Wavelength Range(A)
1	6.78	5.01	2850-5350
2	13.67	2.45	3375-4825
3	20.75	1.57	3600-4600
4	28.20	1.11	3720-4480
5	36.20	0.81	3795-4405
6	45.13	0.59	3850-4350
7	55.78	0.41	3895-4305
8	70.90	0.21	3945-4255

ıotographic plates were used. These were developed for 3 in with continuous agitation at 68°F in DK-19. The nulsion was calibrated by a two-step filter, preliminary ırve method *(5)*. Photometric measurements were made ith a Jarrell-Ash Model 2100 microphotometer.

Spectral line widths were generally measured with a avelling miscroscope, but in some cases the spectra were ojected on a screen and the line widths measured with a ıthetometer.

Experimental

One of the features of the Ebert mount appears to be ıe ease with which wavelength region change can be ac- omplished by simply rotating the grating about its vertical ‹is to bring various wavelengths to focus on the photo- aphic plate. Since the dispersion of the grating is de- endent wholly upon the angle of incidence for any ırticular wavelength at the centre of the plate, a series dispersions are readily available by turning the grating various angles corresponding to the various orders of ıat particular wavelength.

Table I illustrates the dispersions available in the first eighth orders for the 4000 A line at the center of the ate. As the dispersion increases the wavelength range ailable on a 20-in. plate will, of course, decrease.

Grating angles as high as 60° have been employed by ıe authors and the resultant spectra were found always to in focus without having to make any adjustments at the it or at the photographic plate. We understand, however, ıat this is not always the case, and, depending on the ating used, minor adjustments are sometimes necessary keep the spectra in focus as the grating angle is in- eased.

ABLE II. A Comparison of the Wavelengths at the entre of the Plate in the Wadsworth and Ebert Mountings

eneral grating equation: $n\lambda = a (\sin i \pm \sin \theta)$
ɔr the central ray: Wadsworth Mount, $\theta = O$ and $n\lambda = a\sin i$
ıd Ebert Mount, $\theta = i$ and $n\lambda = 2 a\sin i$.

Wavelength at Center, A

i	Wadsworth[a]	Ebert[b]
8°	2359	4712
10°	2943	5881
12°	3524	7041
14°	4100	8190
16°	4672	9329
18°	5238	10463
20°	5797	11583
24°	6894	13772
28°	7958	15900
32°	8981	17910
36°	9963	19903

rom (12)
rom table supplied with Ebert spectrograph

As the angle of incidence is increased the effective aperture presented by the grating to the collimator decreases according to the cosine of this angle. Thus at an angle of 60° only one half of the available light is incident on the grating. This loss in intensity can be remedied to some extent by increasing the slit width (usually with a corresponding loss in potential resolving power), or by employing a grating especially blazed for the particular wavelength region under study.

Much higher wavelengths are available than are practical with a Wadsworth mount of the same focal length, not only because the grating can be readily turned to very high angles, but also because identical angles of incidence yield twice the wavelength at the center of the plate in the Ebert mount. This is immediately obvious when the general grating equation is applied to both systems (Table II).

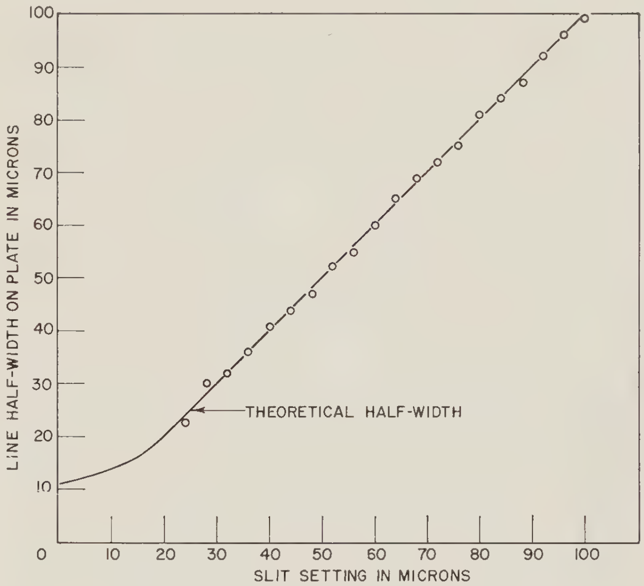


Fig. 2. Variation of Line Half-Width with Increasing Slit Width (Cd 3500.00 A)

The symmetrical arrangement of the Ebert mount results in an essentially self-correcting system which should produce, at the center of the plate, coma free and almost stigmatic images with a one to one correspondence between the slit and its image on the plate. To partly check this feature the slit was illuminated with essentially non-coherent light by focusing the cadmium vapour lamp on it by a three lens condensing system. The Cd 3500.00 A line was photographed at the center of the plate at various slit settings. The results are illustrated in Figure 2. The dots on the graph represent experimental results. The solid line represents the theoretically half-widths which were calculated according to van Cittert *(6)*. Thus we see that for line widths which we could conveniently measure (24μ and greater) there was no comatic effect. A more thorough evaluation of coma in the instrument is presented below.

As the image moves away from the center of the plate the correcting effects should become less effective. No measurements were made in these regions, but we have found the images even at the extremities of a 20-in. plate to be sharp and quite usable for analytical purposes although, as we shall see, the coma is much increased at low wavelengths and the astigmatism is more pronounced at the edges of the plate.

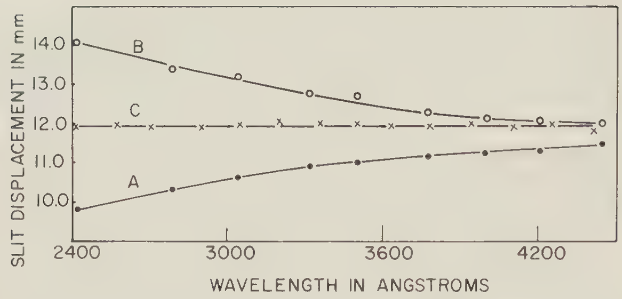


FIG. 3. FOCAL CURVES BY THE METHOD OF SEPARATION OF BEAMS

An exact determination of the focal curve and an evaluation of the coma in the instrument was made using the method of separation of beams as recommended by Arrak *(7,8)*. This was done by dividing the surface of the grating into four equal sections, preparing the three possible masks where nonadjacent areas are left unmasked, and exposing focus plates for each mask in the ordinary way. The focal curves obtained are shown in Figure 3. Curve *C*, which represents light from the two extreme portions of the grating, defines the position of the tangential or principal focus. This is a straight line parallel to the wavelength axis and shows the entire spectrum from 2400 A to 4500 A to be in focus at one slit setting, well within Arrak's criterion *(7)* for proper focussing.

Curves *A* and *B* (Figure 3) are indicative of the extent of coma in the instrument, the vertical distance between the two being equal to half the length of the characteristic focal line, *l*, (the straight line along which the rays of an oblique pencil of light are focussed due to the comatic aberration). From this distance the width, y_o, of the comatic line can be obtained since it is $\frac{1}{2}$ tan $(\alpha/2)$, where α is the angle subtended by the grating at the focal point (tan $\alpha/2$ in our case is equal to 0.0159).

Further, the comatic defocussing factor, $K_c = (\Delta y/y_o)^{1/2}$, was calculated. Δy is the width of the slit image in the absence of aberration and diffraction effects and is equal to the slit width in the case of the Ebert mount. Knowledge of K_c enables one to mask down the grating to that factor without materially reducing the intensity of a

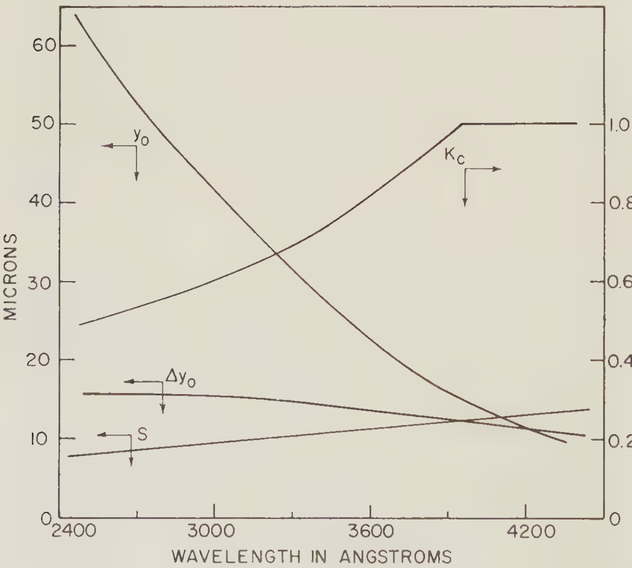


FIG. 4. THE QUANTITIES y_o, Δy_o, K_c, AND S AS A FUNCTION OF WAVELENGTH

line yet reducing the background by a factor $1/K_c$.

Finally, the coma limited slit width,

$$\Delta y_o = \lambda D/K_cR = y_o^{1/3}\lambda^{2/3}D^{2/3}R^{-2/3},$$

was estimated *(8)*. This is the maximum slit width consistent with optimum resolving power and intensity.

The information obtained above has been illustrated in Figure 4. Also shown is the optimum slit width, S, for the instrument calculated according to Schuster (9), $S = \lambda F/A$, where F is the focal length of the collimator and A its effective aperture. It is evident that the optimum slit setting is governed by Δy_o below 3930 A and by S above this wavelength.

Theoretically, curves *A*, *B*, and *C* should intersect at that point in the spectrum which is coma free. For the Ebert mount this should be in the centre of the plate as mentioned above. Arrak *(10)* has suggested that the fact that the experimental curves do not behave in this manner could be due to an error of run in the grating. Behaviour

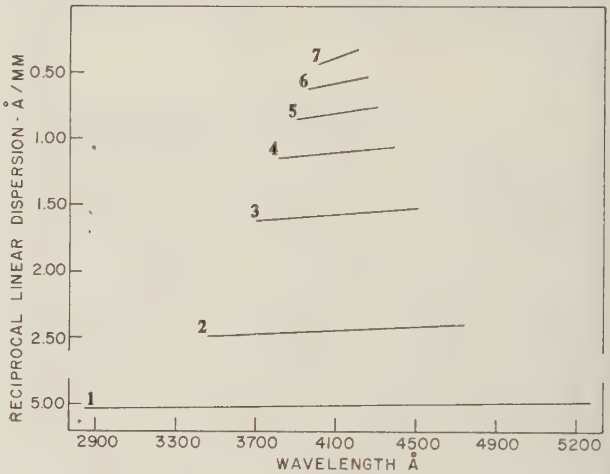


FIG. 5. VARIATION OF RECIPROCAL LINEAR DISPERSION IN DIFFERENT ORDERS ACROSS A 20-IN. PLATE

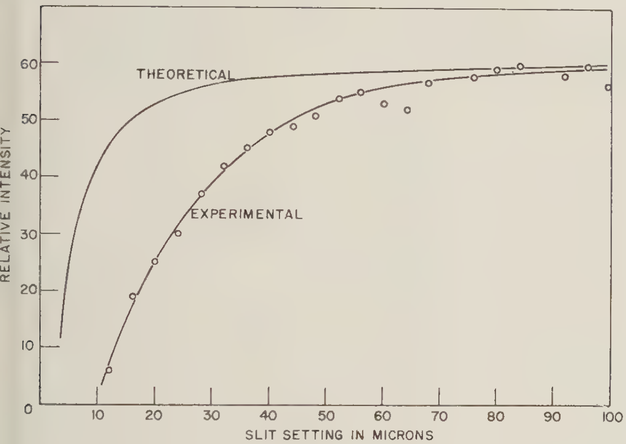
of the curves near the high wavelength end of the plate suggests further that this error of run is not uniformly progressive. Because of this, and since the mirror in the instrument could not be easily rotated about its vertical axis, no attempt was made to cancel the effect by mounting the mirror in aberration.

The dispersion at any point in the focal plane is dependent on the angle of diffraction. Since the angle of diffraction varies across the plate the dispersion can vary considerably, as is indicated in Figure 5 that shows the deviation in dispersion for the first to seventh orders across a 20-in. plate centered at 4100 A. The deviation is almost negligible in the first order visible and ultraviolet regions, amounting to only about 1.5% across the plate. However, at higher grating angles this deviation becomes progressively greater. For example, when working in the 20,000 A region at an angle of 36° the variation across the plate is approximately 10%, and in the 30,000 A region at an angle of 62° it is as high as 22%. This can be quite a handicap when first exploring a new wavelength region in the higher orders and necessitates the production of wavelength calibration plates (we use an iron spectrum) for each region.

At high grating angles the individual spectral lines have an appreciable tilt. This could be quite an inconvenience if the microphotometer available has no provision for altering its slit to match the tilt of the spectral line.

›therwise, the spectrograph slit itself must be tilted equally 1 the opposite sense to bring the lines vertical on the plate, 1 adjustment which has no effect on the definition and esolution of the instrument *(4)*.

Schuster *(9)* and many other workers have generally ecommended a slit width $S = \lambda F/A$ as the best com-romise combining good intensity with little loss in re-›lving power. Godfrey *(11)* has shown that as a slit, luminated with noncoherent light, is opened, the intensity f a line increases very rapidly at first, followed by a slow se. At the recommended slit width the intensity is about 5% of that of a very wide slit and there is about a 20% ›ss in maximum resolving power. Increasing the slit width eyond this point should result in but little increase in ıtensity and a marked decrease in resolving power. For ur spectrograph illuminated with noncoherent light at 500 A this slit width is 11μ and if the effect of coma is onsidered, 14μ.



'IG. 6. VARIATION OF LINE INTENSITY (Cd 3500.00 A) WITH INCREASING SLIT WIDTH

It was noted, however, that intensities with this instru-ıent were extremely low at this slit setting and opening he slit further resulted in a great gain in intensity. Fol-›wing this observation measurements were made to in-estigate the variation in intensity of the Cd 3500.00 A ne with changing slit width. Measurements were made sing essentially noncoherent light. The results of this vork are shown in Figure 6. The actual intensities have een altered so that the maximum in both cases is roughly he same and a smooth curve has been drawn in spite of he fact that the deviations from the curve are fairly re-roducible. The apparently great deviation from ideality is triking. It has been suggested that this may be due to oma and deformation of wavefronts as a result of small nperfections in the optics.

A similar series of measurements made with a Hilger ırge Littrow quartz spectrograph whose slit was illumi-ated with coherent light gave an intensity curve very lose to the theoretical curve for this type of illumination. ıttempts to carry out a series on another grating spectro-raph were unsuccessful, since one could not be located in his area with a continuously variable slit. However, three oints were measured using a fixed slit mechanism on a .4-m Wadsworth spectrograph, and while the results were oo few to be conclusive, there were indications of large eviations from ideality with this grating instrument also. Noncoherent light was employed in the latter case.

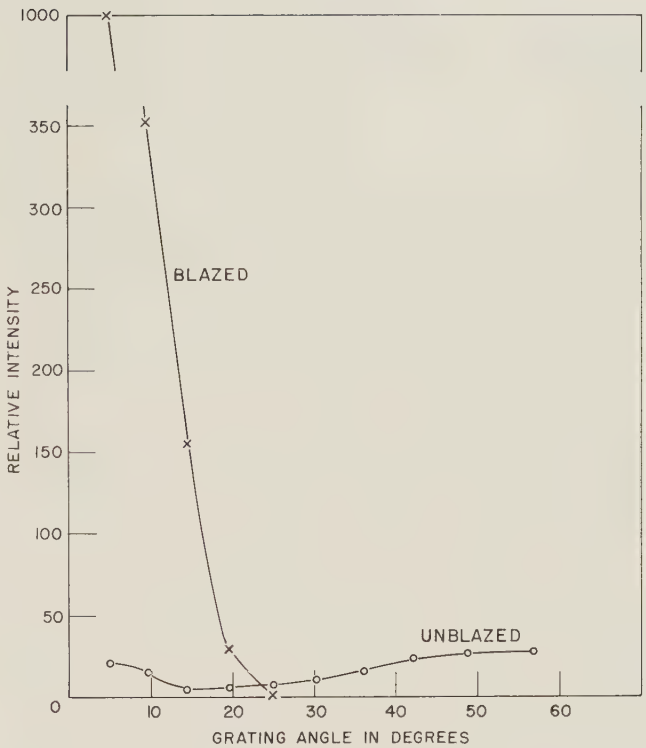


FIG. 7. VARIATION OF LINE INTENSITY (Cd 2836.907 A) IN DIFFERENT ORDERS ON BOTH SIDES OF THE GRATING NORMAL

As Figure 6 indicates, this deviation represents a considerable loss of energy at low slit settings, a loss which is emphasized when working in the higher orders where the light intensity is inherently low because of the small proportion of light diffracted into these orders by an ordinary grating (see below). In these regions it becomes necessary to use large slit widths in order to obtain useful intensities, resulting both in a loss in resolving power and an increase in background radiation.

Figure 7 shows the variation in intensity of the Cd 2836.907 A line as the angle of incidence was changed to bring the first to tenth orders of this line to the center of the plate. Since the grating supplied with the instrument was blazed to diffract the great majority of the energy into the first and second orders of the ultraviolet and visible regions the intensity from the blazed side drops off very quickly as the angle of incidence is increased, so that at 25° it is already negligible. However, for any blazed grating there are angles on the other side of the grating normal (the unblazed side) which should also give a fair distribution of intensities. The reflectivity is much poorer on the unblazed side, but as Figure 5 indicates, it is possible to get useful intensities at quite high angles. (The intensities would be even higher than indicated were it not for the fact that the effective aperture of the instrument decreases with increased angle of incidence.) In our work with angles greater than 23° we always use the unblazed side of the grating. This is achieved with the Ebert mount by simply rotating the grating in a counterclockwise direction rather than the normal clockwise direction.

Although the intensity in the higher orders (unblazed side) is about one fortieth of that available in the first order (blazed side), in general practice the ratio is really not that great since we have found it necessary to screen out at least 90%, and quite often 97%, of the light when handling normal analytical samples excited in the dc arc

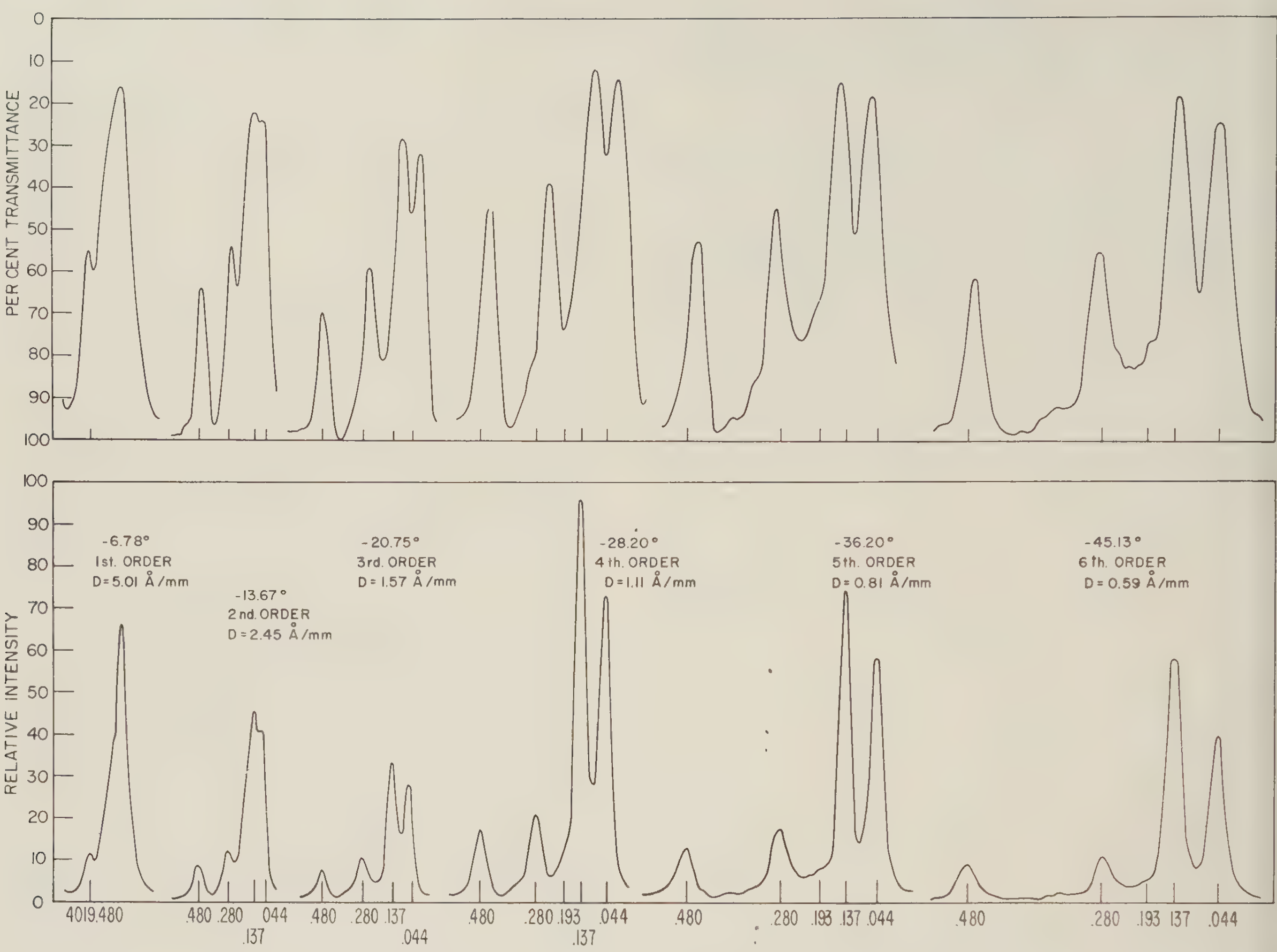


FIG. 8. THE 4019 A GROUP: FIVE % THORIA IN CERIA, ORDERS ONE TO SIX (UNBLAZED)

in the first order. Taking this factor into consideration, the useful intensity in the first order (blazed) is really only 1 to 4 times that in the higher orders (unblazed). This discrepancy can usually be compensated for by using larger samples and/or slit widths. Of course, ideally, for work in the higher orders a grating blazed for that region should be used.

Some work which we have done concerning the determination of thorium in ceria may serve as an illustration of the type of work which may be done in the higher orders and also point out the severe limitation set by the dc arc or ac spark to high dispersion work.

The most sensitive and persistent thorium line at 4019.137 A can seldom be used for analytical purposes at dispersions normally available in the first and second orders because of close lying interfering lines due to the many elements generally associated with thorium. In this particular case there are two cerium lines nearby: a strong line at 4019.044 A and a rather weak one at 4019.193 A. To resolve these lines, according to the Rayleigh criterion, requires a resolving power of some 72,000 which should not be very difficult with an effective 62,000 line grating. Indeed, they are adequately resolved in the second order using a 15μ slit, but the background is so high in this order as to render the thorium line analytically useless. Increasing the dispersion should lead to a higher line to background ratio, since the background will decrease inversely with the dispersion, and, also, the greater resolution obtained should facilitate photometric measurements. To obtain, with our grating, useful intensities in orders higher than the second in the 4000 A region necessitated using the unblazed side of the grating normal, and, because of the lower inherent intensities in these regions, wider slit widths.

The top half of Figure 8 shows the microphotometric traces obtained in the first to sixth orders of the 4019 A group using a 30μ slit and the unblazed side of the grating normal. The sample consisted of 1 mg of ceria containing a 5% thoria impurity, burned to completion in a dc arc. The "order sorter" was used in this work to offset spurious lines from other orders and to produce lower backgrounds by the removal of superfluous overlapping spectra.

In the lower half of Figure 8 the transmittance values have been converted to intensities to present a clearer picture of the situation. The group consists of four cerium lines and the thorium line. The Ce 4019.193 A line is not very evident because of its low intensity but its position has been marked in the higher orders. Using the 30μ slit, this line is not resolved from the thorium line until the fourth order, corresponding to a reciprocal linear dispersion of 1.11 A/mm, is reached. These lines could have been resolved in the third order using a smaller slit width, but the grating

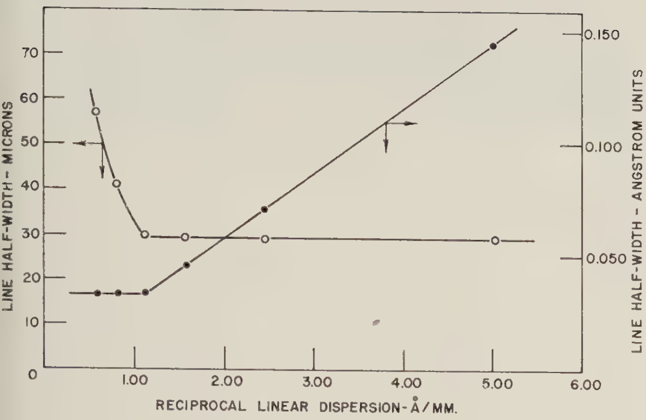


Fig. 9. Variation of Line Width (Ce 4019.480 A) with Reciprocal Linear Dispersion

does not yield good intensities in this region on either the blazed or unblazed sides of the grating normal.

Beyond the fourth order, the line intensities decreased, and although this is not readily evident to the eye, the line widths broadened.

The half-widths of the Ce 4019.480 A line were measured and were found to equal the spectrograph slit width of 30μ in the first four orders (Figure 9) but then increased in the fifth and sixth orders proportionally with the decrease in reciprocal linear dispersion. The same data were plotted to represent the half-widths of the line in angstrom units on the plate. Beyond the fourth order the actual half-width of the line in angstroms was constant.

These observations would indicate that at reciprocal linear dispersions of 1.11 A/mm and smaller the spectrograph 30μ slit was no longer the limiting factor in the formation of the spectral line image, since the natural breadth of the line in these cases exceeded the width of the image of the slit on the photographic plate, and the image on the plate was that of the spectral line itself and not of the slit. Since there is a one-to-one correspondence between image and object in this spectrograph it may be assumed that the natural half-width of the Ce 4019.480 A line under the conditions of excitation which prevailed in the dc arc was 0.033 A. Once the natural line half-width has exceeded the width of the slit image on the plate the sensitivity of the line, as expressed by the intensity of its peak height, must decrease with increasing dispersion, since the increased dispersion can only serve to spread the spectral line intensity over a greater plate area. Of course, intensity can always be regained by opening the slit so that its image is equal to the spectral line width, but sensitivity cannot be improved since the background will increase by the same factor, maintaining the identical line-to-background ratio. A still further increase in slit width not only reduces the resolution but also decreases the line-to-background ratio.

The maximum resolution obtainable is always limited by the natural half-width of the spectral lines under consideration. The natural breadth of these lines is dependent upon several factors, but in high temperature sources the most predominant by far is the Doppler broadening due to the random variations of velocity possessed by the emitting atoms with respect to the line of sight of the spectrograph.

In the case of cerium, as has just been demonstrated, the line half-widths are of the order of 0.033 A. Using the Rayleigh criterion it follows that lines in the cerium spectrum closer than about 0.04 A cannot be resolved, regardless of the resolving power of the spectrograph. This means that in the 4000 A region the maximum resolving power obtainable is of the order of 100,000 in spite of the fact that our instrument has a theoretical resolving power of 250,000 in the fourth order and 370,000 in the sixth.

The above example of thorium in cerium is almost an optimum case since we were dealing with relatively heavy metals and the Doppler broadening varies inversely with the square root of the mass of the emitting atom. The spectral lines of the lighter elements have considerably greater half-widths when excited in the dc arc.

Some observations made in the determination of boron in steel bear this out. Although precise measurements were not made, it was noted that with a slit of 15μ the boron lines were broadened even in the first order at a dispersion of 5 A/mm and the iron lines were broadened in the second order at a dispersion of 2.5 A/mm. This indicated that the half-widths of the lines of these elements when excited in the dc arc were respectively greater than 0.075 A and 0.04 A. Accepting this value indicated that in an iron spectrum lines closer than 0.05 A could never be resolved under these conditions and the most sensitive boron line at 2497.733 A would always be analytically useless due to the neighbouring iron line at 2497.720 A.

It should be mentioned that at times it was found advantageous to work with low slit widths in the higher orders, sacrificing sensitivity in order to gain photometric precision due to lower backgrounds.

Literature Cited

(1) H. Ebert, Wiedemanns Ann. **38,** 489 (1889)
(2) W. G. Fastie, J. Opt. Soc. Am. **42,** 641 (1952)
(3) W. G. Fastie, H. M. Crosswhite, and P. Gloersen, Ibid. **48,** 106 (1958)
(4) R. F. Jarrell, Ibid. **45,** 259 (1955)
(5) G. V. Wheeler, APPLIED SPECTROSCOPY **10,** 11 (1956)
(6) P. H. van Cittert, Z. Phys. **65,** 547 (1930)
(7) A. Arrak, Spectrochim. Acta **12,** 1003 (1959)
(8) A. Arrak, Ibid. **12,** 1015 (1959)
(9) A. Schuster, Astrophys, J. **21,** 197 (1905)
(10) A. Arrak, Private communication
(11) G. H. Godfrey, Australian J. Sci. Res. **1,** 1 (1948)
(12) G. R. Harrison, R. C. Lord, and J. R. Loofbourow, *Practical Spectroscopy,* Prentice-Hall, New York, 1948

Submitted February 4, 1960, revision received July 17, 1961

Far Ultraviolet Spectroscopy. II. Analytical Applications

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Abstract

One of the prime requirements for the use of a spectral region for analytical purposes is a library of reference spectra. Since no adequate libraries exist, the literature since 1941 has been indexed and references to spectra are listed by empirical formula. The few published analytical applications of far ultraviolet spectroscopy are discussed. With the commercial spectrophotometers that are now available it seems certain that the analysts will make frequent use of this region in the future.

Introduction

The high absorptivities of most compounds and the characteristic spectra of many gases in the far ultraviolet region make this region very attractive for analytical purposes. However, to date few analytical applications have been published. The reasons for this probably reside in the instrumental difficulties of obtaining good spectra. Working in the region below 1600 A still requires extensive experimental labor; however, the region from 1600 to 2200 A may now be studied with relative ease and quantitative accuracy. This paper attempts to point out the types of analytical applications that may utilize the far ultraviolet region.

In the previous paper in this series the modifications necessary to operate a Beckman DK spectrophotometer to 1700 A were outlined *(89a)*. Other instruments capable of operation in the far ultraviolet are made by Hilger and Watts Ltd., London, England, Jarrell-Ash Co., Newtonville, Mass., and Paul M. McPherson, Acton, Mass. The major innovation of the Beckman instrument is automatic recording of relative transmittance (or absorbance) versus wavelength.

A number of good reviews of far ultraviolet instrumentation have appeared *(33,75,149,162,204)*. The major problems of far ultraviolet absorption spectroscopy are concerned with the source of radiation, window materials, and mirrors. The absorption of air calls for special precautions. Most of the far ultraviolet instruments in existence evacuate the monochromator and use gratings to disperse the radiation. The Beckman instrument, on which the spectra shown here were obtained, is purged with nitrogen and utilizes a special purity quartz prism. The performance of the published instruments varies widely, and few of the publications discuss such vital matters as stray light, linearity, response, time, etc.

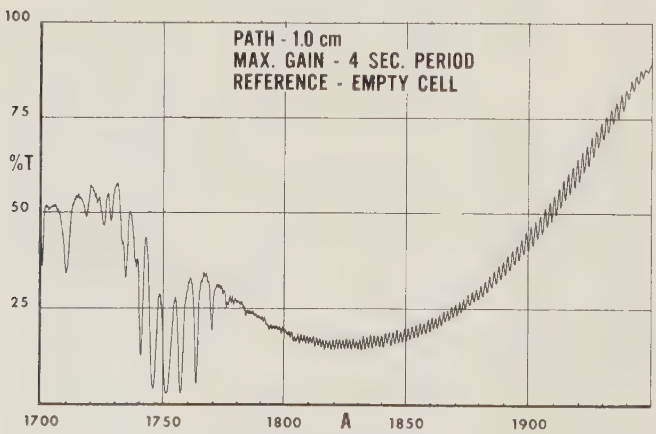

FIG. 1. SPECTRUM OF IODINE VAPOR

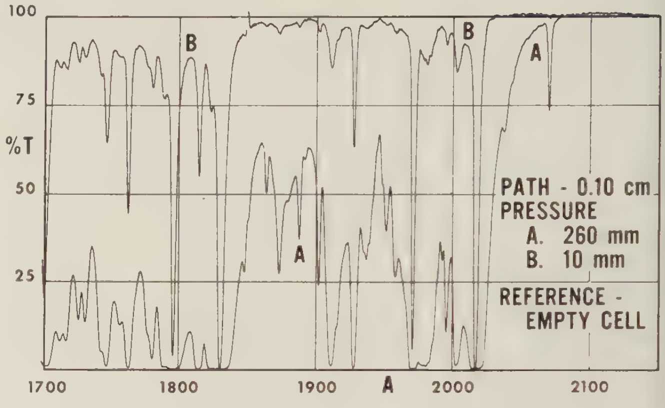

FIG. 2. SPECTRUM OF METHYL IODIDE VAPOR

The Absorption Process

Absorption of far ultraviolet radiation occurs through electronic transition of molecules and atoms. Vibrational and rotational transitions may be super-imposed on the electronic and are responsible for much of the fine structure in the vapor spectra. As shorter wavelengths are used the molecules will be excited to higher states and ultimately be dissociated and ionized. Spectra may be in the form of continua, diffuse, or sharp bands with spacings that may be correlated with vibrational modes. Frequently the absorption bands become sharper on going to shorter wavelengths. The spectrum of iodine vapor is shown in Figure 1, which illustrates the nature of far ultraviolet spectra. Cordes has analyzed this spectrum *(25)*, and the multi-structured band centered at 1825 A would appear as a continuum at lower resolution. This spectrum is exceedingly easy to obtain, since there is just the proper vapor pressure from the iodine crystal at room temperature to produce 20-80% absorption in a 1 cm cell. Of course the air must be displaced by a transparent gas.

Electronically excited states are readily perturbed by neighboring molecules; hence the spectra of liquids and solids are seldom as discrete as the spectra of vapors. The radius of the electron cloud is greater in the excited state than in the ground state. Thus the vibrational and rotational structure is almost always lost on going from the vapor to a solution. In this regard the ultraviolet spectra are influenced to a much greater extent by solvents than are infrared spectra. Figures 2 and 3 illustrate this. In Figure 2 we see the complex spectra of methyl iodide. Sponer and Teller have reviewed the earlier studies on this compound *(173)*. The strong band at 2012 A arises through excitation of the molecule from the ground state to a first excited electronic state. The other bands between 1850 and 2012 A correspond to excitation at higher states that correspond to the same electronic plus vibrational states. The most pro-

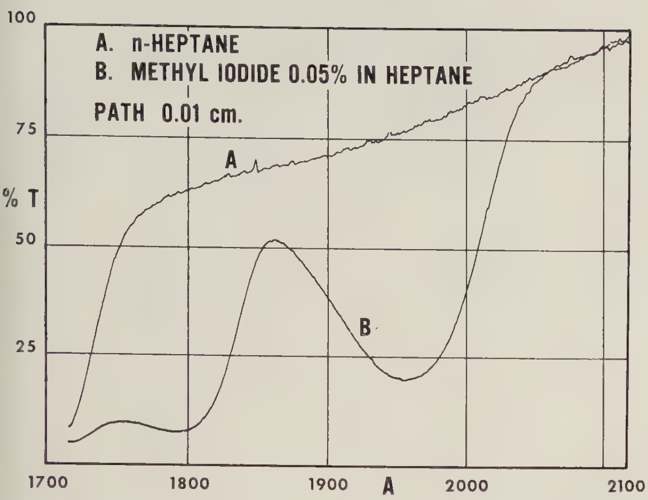

Fig. 3. Spectrum of Methyl Iodide Solution

nounced spacing between these bands is 1090 cm^{-1}. Bands representing one, two, and three quanta of this vibrational transition are evident. The band at 2064 A is interesting, since it arises through absorption of energy by a vibrationally excited state. Intensity of this band is strongly dependent on sample temperature, because the number of molecules in the vibrationally excited state is dependent on temperature. Absorption of light in the region 1700-1830 A arises through excitation to a next higher electronic state accompanied by vibrational fine structure. The separation of the most pronounced bands in this group corresponds to a vibration of 1080 cm^{-1}.

Figure 3 shows the spectra of the methyl iodide dissolved in heptane. All of the vibrational fine structure is gone, and we see only two broad bands corresponding to excitation to the first two electronic states.

While ultraviolet absorption bands are not so easily identified with specific molecular groups as are infrared vibration bands, one can often attribute absorption at a given wavelength to a specific group and to a specific atom. Thus in the vapor phase all olefins absorb around 1800 A. Ketones absorb at 1950 A. Organic iodides absorb around 2000 A. Bromides absorb around 1850 A. Inorganic iodides in aqueous solution absorb at 1950 and 2250 A. Replacement of hydrogen in an absorbing molecule by CH_3 or some other aliphatic group usually displaces absorption bands to longer wavelengths. Bands may be displaced to longer or shorter wavelengths when dissolved in solvents *(250)*.

In order to make a distinction among individual molecules within a class such as between dimethyl and methyl ethyl ketones, it is necessary to examine the vibrational fine structure. Obviously this must be accomplished by examining vapor phase spectra. In the liquid phase only small differences may be seen in the exact position of the band maxima.

A number of reviews of the absorption process occurring in ultraviolet spectra may be found *(17,88,129,130, 150,199,215)*.

The intensities of far ultraviolet bands (above 1700 A) at their maxima generally run from 2000-120,000 L/mol-cm or 90-5400 cm^{-1}. A few representative values are given in Table I. The values are for vapor phase spectra except for naphthalene and anthracene. The agreement among published intensity values on the same compound is rather poor. Jones and Taylor show values differing by ±39% *(88)*. This is probably due to varying resolution among the instruments used, although the conditions of pressure and temperature have an effect on absorptivity.

The calculation of minimum detectable concentration or pressures may be interesting. A gas having an absorptivity of 5000 cm^{-1} would absorb 2% of the light (A = 0.01) in a 2 m path (typical optical path through a Littrow monochromator of 50 cm focal length) at a pressure of 10^{-8} atm. If such a gas were present in a nonabsorbing matrix such as nitrogen, hydrogen of the noble gases, one could easily detect 0.01 ppm. Of course, when one must use a shorter optical path, a less absorbing analyte, or a more absorbing matrix, the sensitivities may be considerably reduced.

Reference Spectra

Possession of a "library" of reference spectra is usually a prerequisite for widespread use of a spectral region for analytical purposes. Unfortunately there are no libraries of far ultraviolet spectra equivalent to the one of the American Petroleum Institute or Friedel and Orchin* collections of near ultraviolet spectra. A few publications contain limited collections. The atmospheric gases have been reported by Watanable *et al (220)*. Jones and Taylor reported the spectra of many unsaturated and aromatic hydrocarbons *(88)*. Klevens and Platt recorded many solution spectra *(248)*, and Ley and Arends studied a number of solutions to about 1850 A *(99)*. However, for the spectra of many compounds one must go to original publications. Fortunately, the review articles by Sponer and Teller cover the inorganic compounds reported prior to 1941 *(173)*. The review of Platt and Klevens itemizes the organic compounds studied prior to 1944 *(129)*.

Table I. Molar Absorptivities in the Far Ultraviolet Region

Compound	*L/mol-cm*	*Wavelength, A*	*Reference*
	Olefins		
Ethylene	33,000	1704	237
Propylene	13,000	1710	88
	Dienes		
1-*trans*-3-Pentadiene	27,500	2148	88
	Aromatics		
Benzene	109,000	1791	88
Naphthalene	122,000	2210	88
Anthracene	21,500	1885	88
	Aldehyde and Ketone		
Formaldehyde	18,000	1750	43
Acetaldehyde	10,000	1815	97
Acetone	9,000	1950	97
	Ethers		
Diethyl ether	2,000	1880	66
Divinyl ether	15,600	2030	66
Furan	31,000	1915	221
	Halogens		
Methyl iodide	20,000	2013	6a
Ethyl bromide	10,000	1700	6a
	Miscellaneous		
Oxygen	500	1700	219
Water vapor	3,000	1700	218
Nitric oxide	900	1830	220
Ammonia	12,000	1940	220

*R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley & Sons, New York, 1951

Tables II and III list references to far ultraviolet absorption spectra of compounds by empirical formula. With a few exceptions only the papers appearing since 1941 are included. The inorganic compounds are given in Table II, and organic compounds are listed in Table III. All compounds containing carbon are listed as organic except for a few carbonates. In order to conserve space, isotopic (except deuterium) and some types of isomeric compounds are not listed separately. Compounds not readily classified by empirical formula (mixtures and polymers) are listed at the end by common name.

Unfortunately, the experimental difficulties in obtaining far ultraviolet spectra have forced the publication of many rather poor spectra. Anyone using the published spectra must consider the possibility of large amounts of stray light. Resolution varies drastically among instruments used by different authors. Many spectra below 1650 A have been deduced from absorption data obtained at certain discrete emission wavelengths of the source used. Absorption information at intermediate wavelengths may be completely unknown.

TABLE II. REFERENCES TO FAR ULTRAVIOLET SPECTRA OF INORGANIC COMPOUNDS

Formula	*Name*	*State*	*λ, A*	*Reference*
A	Argon			203
AgBr	Silver bromide	Film	800-1600	95
AgCl	Silver chloride	Film	800-1600	95
		Film	1100-2000	169
Al	Aluminum	Film	60-220	183
		Film	150-400	3
		Film	450-1250	208
AlF	Aluminum monofluoride	Vapor		9
		Vapor	1250-2000	11
		Vapor	1300-2000	164
$Al_2F_2SiO_4$	Topaz	Solid	1550	22
Al_2O_3	Sapphire	Solid	1500-2100	13
		Solid	1425	22,45
		Solid	1500	55,56,90
BF	Boron monofluoride		1900-2100	21,125
$B_3H_3N_3Cl_3$	B-Trichlorazole	Solution	1700-2300	153,248
$B_3H_6N_3$	Borazole	Solution	1700-2250	131,248
$BaCl_2$	Barium chloride	Solid	1100-1800	169
BaF_2	Barium fluoride	Solid	1345	23
Be	Beryllium	Film	60-220	183
Bi	Bismuth	Film	475-1250	207,208
BrH	Hydrogen bromide	Vapor		142,154b,156
BrF	Bromine fluoride	Vapor	1560-1760	19
Br_2	Bromine	Solution	1850-2200	14
CaH_4SO_5	Gypsum	Solid	1620	22
$CaCl_2$	Calcium chloride	Solid	1100-1800	169
CaF_2	Calcium fluoride	Solid	1100-1600	22,55,56,90, 94,167,169
ClH	Hyrogen chloride	Vapor	1350-2100	142,154a,156
Cl_2	Chlorine	Vapor	1070-2100	98
Cs	Cesium	Film	1850-4400	233
CsBr	Cesium bromide	Solid	1100-2000	169
CsCl	Cesium chloride	Solid	1100-1800	169
CsF	Cesium fluoride	Solid	1100-1600	169
Cu	Copper	Vapor	1200-1430	52
$CuCl_2$	Copper chloride	Solid	1100-2000	169
D_2	Deuterium	Vapor	1215	246
FH	Hydrogen fluoride	Vapor	1540-1820	157
		Vapor	1500-1650	166
F_2	Fluorine	Vapor	807-1036	73
Ga	Gallium	Vapor	1500-1650	47
GeO	Germanium oxide	Vapor	1250-2000	9,10,163
H_2	Hydrogen	Vapor	400-1300	20
		Vapor	480-880	134,188
		Liquid	1300-	203
He	Helium	Vapor	504	7,120
Hg	Mercury	Vapor	1849	216
		Solution	2537	127
$HgBr_2$	Mercuric bromide	Vapor	1813-1861	173
$HgCl_2$	Mercuric chloride	Vapor	1670-1730	173

TABLE II. REFERENCES TO FAR ULTRAVIOLET SPECTRA OF INORGANIC COMPOUNDS—*(Continued)*

Formula	*Name*	*State*	*λ, A*	*Reference*
IH	Hydrogen iodide	Vapor		142,154b,156
I_2	Iodine	Solution	1850-2200	14,59b
		Vapor	1500-1950	25
In	Indium	Vapor	1650-1757	48,242
		Vapor	1758	111
		Film	475-1230	207,208
K	Potassium	Film	1850-3150	233
KBr	Potassium bromide	Solid	1100-2000	22,169
		Solid	1700-2500	198
KCl	Potassium chloride	Solid	1100-1800	169
		Solid	1750	22
		Solid	1850-2300	41,126
		Film	950-1700	67
KF	Potassium fluoride	Solid	1100-1600	169
KI	Potassium iodide	Solid	1100-2400	169
		Solid	1700-2500	198
$KMg_3AlSi_3O_{10}F_2$	Mica	Solid	2000	136
Li	Lithium	Film	1850-2050	233
LiBr	Lithium bromide	Solid	1100-2000	169
LiCl	Lithium chloride	Solid	1100-1800	169
LiF	Lithium fluoride	Solid	1000-	22,169
		Solid	1200-1600	167,168
		Solid	1500-	55,56,82
LiI	Lithium iodide	Solid	1100-2400	169
Mg	Magnesium	Vapor	1620	29
		Film	120-300	183
$MgAl_2O_2$	Spinel		1840	90
$MgBr_2$	Magnesium bromide	Solid	1100-2000	169
$MgCl_2$	Magnesium chloride	Solid	1100-1800	169
MgF_2	Magnesium fluoride	Solid	1100-1400	37,169
MgO	Magnesium oxide	Solid	1600-3200	87
		Solid	900-2100	154
N	Atomic nitrogen	Vapor	400-750	40
NH_3	Ammonia	Vapor	374-1300	178
		Vapor	850-2300	36
		Vapor	1050-2150	220
		Vapor	1590-2570	196
		Solution	1800-3000	99
NH_4Cl	Ammonium chloride	Solution	1800-3000	99
NO	Nitric oxide	Vapor	150-1100	59
		Vapor	374-1300	179
		Vapor	1050-2300	109,112,220
		Vapor	1300-1500	187,189, 190,202
		Vapor	1670-	12,15,70, 181,231
		Solid	1600-2400	58
NOCl	Nitrosyl chloride	Vapor	1000-2200	144
NO_2	Nitrogen dioxide	Vapor	1000-2200	144
		Vapor	1080-2700	119
		Vapor	1350-2050	116,117
NS	Nitrogen sulfide	Vapor		35
N_2	Nitrogen	Vapor	150-1000	6,27
		Vapor	300-1300	222
		Vapor	750-990	234,235,236
		Vapor	900-1050	135
		Vapor	1000-2000	171,184, 193,230
		Vapor	1215.7	140
		Vapor	1689-1729	256
		Liquid		203
N_2O	Nitrous oxide	Vapor	167-1000	4
		Vapor	1080-2100	220,238
		Vapor	1400-2100	155,159
		Solid		57,160
N_2O_2	Nitrogen dioxide	Solid	1600-2400	58
Na	Sodium	Vapor	1600-2412	30
		Film	1850-2100	233
$NaHCO_3$	Sodium bicarbonate	Solution	1800-3000	99
NaBr	Sodium bromide	Solid	1100-2000	169
		Solid	1700-2500	198
NaCl	Sodium chloride	Solid	1100-1800	169
		Solid	1750-2200	22,41
		Film	950-1700	67
NaF	Sodium fluoride	Solid	1100-1600	169
NaI	Sodium iodide	Solid	1100-2400	169
		Solid	1700-2500	198

Table II. References to Far Ultraviolet Spectra of Inorganic Compounds—*(Continued)*

Formula	*Name*	*State*	*λ, A*	*Reference*
NaK	Eutectic	Liquid	2100-3400	172
Na_2CO_3	Sodium carbonate	Solution	1800-3000	99
OD_2	Heavy water	Liquid	1850-1900	239,251
OH_2	Water	Vapor	160-1100	5
		Vapor	160-2000	84
		Vapor	200-500	2
		Vapor	900-2000	72
		Vapor	1060-1860	218,220
		Vapor	1215	140
		Vapor	1400-2000	225
		Vapor	1600-2001	65,79,80,81,83
		Liquid	1700-	90,239,251
O_2	Oxygen	Vapor	100-1000	1
		Vapor	200-1320	135
		Vapor	300-1300	223
		Vapor	650-	141,185
		Vapor	1000-1300	191
		Vapor	1000-2000	171,219,220
		Vapor	1200-1500	217
		Vapor	1215	140
		Vapor	1300-1800	31,96,59a
		Vapor	1750	16,18,93,254,255
		Vapor	1920-	26,50,152
		Solution	1900-2400	68,118
		Solid	1500-2000	161
O_3	Ozone	Vapor	526-1305	123
		Vapor	1000-2200	144,192,220
		Vapor		34,85
PO	Phosphorous oxide			35
PS	Phosphorous sulfide			35
P_2	Phosphorous			35,241
Rb	Rubidium	Film	1850-3600	233
RbBr	Rubidium bromide	Solid	1100-2000	169
RbCl	Rubidium chloride	Solid	1100-1800	169
RbF	Rubidium fluoride	Solid	1100-1600	169
RbI	Rubidium iodide	Solid	1700-2500	198
S	Sulfur	Vapor	1650-1850	106,107,224
SH_2	Hydrogen sulfide	Vapor	1200-2000	148
SF_6	Sulfur hexafluoride	Vapor	780-1850	101,121
SO_2	Sulfur dioxide	Vapor	1000-3000	143
		Vapor	1650-2200	62
SeH_2	Hydrogen selenide	Vapor	1200-2000	148
Si	Silicon		1000-2000	171
SiF	Silicon monofluoride	Vapor	1870-1960	86
SiO	Silicon monoxide	Vapor	1250-2000	9,10
		Film	150-1200	3
			1250-2000	163
SiO_2	Silica	Fused	1463-1633	22,163
		Fused	1600-2200	13,28,44,46,90
SiO_2	Quartz	Crystalline	1463-1633	139
			1500-	38,46,81,90,113
			1850	24
Sn	Tin	Vapor	1600-1800	49,51
		Film	450-1230	207,208
SnO	Stannous oxide	Vapor	1250-2000	9,10
SnS	Stannous sulfide	Vapor	1500-2000	8,9
TeH_2	Hydrogen telluride	Vapor	1200-2000	148
Tl	Thallium	Vapor	1450-2030	110
$ZnCl_2$	Zinc chloride	Solid	1100-2000	169

Technique

The problem of obtaining good spectra to 1700 A is not much different from that of near ultraviolet spectra, but one must give added attention to cell matching and solvent purity. As one proceeds to shorter wavelengths, technical difficulties increase. Of course, atmospheric absorption must be eliminated either by purging or evacuation. There are no serious problems with containment of the sample when working to 1650 A or even to 1200 A with good lithium fluoride windows; however, in some cases the sample cells must have very short optical paths, and they must not "leak" if placed in an evacuated chamber. Vapors leaking from a sample cell may wander into the reference channel of a double beam instrument causing a marked increase in noise.

When working with liquid samples, one is usually obliged to use very short optical path cells because of the high absorbance of solutes and solvents. The sandwich type cells familiar to the infrared spectroscopists are most useful, since they are readily cleaned and can be easily made into any optical path greater than 0.03 mm. Windows of suprasil, synthetic quartz (plane of the window must be normal to the optic axis), or lithium fluoride may be used. In order to prevent fracturing, the lithium fluoride windows must be thicker than those of silica, and all of the cells studied have shown greater absorption than those of suprasil above 1700 A.

Solutions can be studied to about 1720 A without undue trouble. Fortunately two solvents of widely varying polarity, water and n-heptane, are among the most transparent liquids. Of course they must be pure. The hydrocarbons are most easily purified by passage through a column of activated silica gel *(90,91)*. The oxygen normally dissolved in liquids should be removed *(68)*. Even in a highly refined state all solvents will absorb somewhat; the effect of this residual absorbance may be minimized by using thin optical paths. Figure 4 shows the spectra of several of these solvents in the thinnest practical cell (0.03 mm). In the case of marginal performance with aqueous solutions it may be worthwhile to use deuterium oxide in place of ordinary water. The absorption edge is displaced about 30 A to shorter wavelengths relative to ordinary water. Highly purified perfluorinated solvents can be used to about 1565 A *(91,137)*. However, these materials saturate at very low concentrations, and the cells usually have to be dismantled to clean after use. Argon, nitrogen, and hydrogen may be compressed and cooled to the liquid state and serve as solvents for work to 1300 A *(203)*. Purified methanol may be used to 1850 A and acetonitrile can be used to about 1780 A. Many saturated hydrocarbons may be used; however, the author has found n-heptane best. Higher molecular weight hydrocarbons contain greater concentration of impurities. Lower molecular weight hydrocarbons suffer from volatility. In thin cells highly volatile liquids form bubbles of vapor under the slightest provocation.

Careful attention must be given to the use of reference cells in double beam operation. One must not push the use of solvent compensation beyond the bounds of safe operation with regard to stray light. Thus aqueous solutions in 0.1 mm thickness should not be scanned with a com-

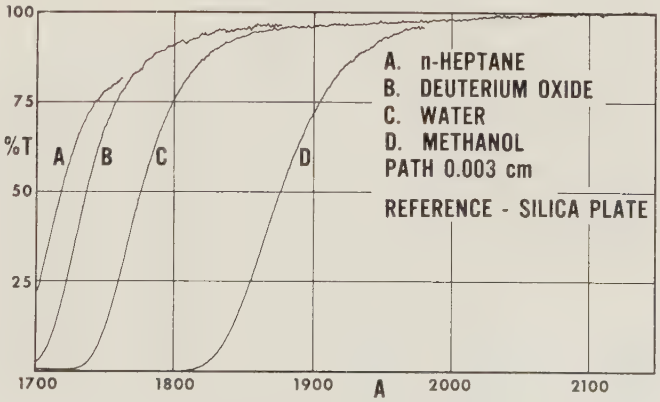

Fig. 4. Solvent Spectra

pensating cell filled with water at wavelengths below about 1770 A in the far uv DK instruments, because the slits will open rapidly and the pen will balance entirely on the stray light signal received by the detector. It is wiser to run such absorbing solutions relative to a silica plate. In this regard it should be noted that the major light losses on passing light through an empty cell are caused by reflection losses from cell surfaces. The refractive index of quartz at 1700 A is 1.72 from which one can compute a reflection loss of 7% at each interface (normal incidence). Since the actual light lost through *absorption* in suprasil windows, 2 mm thick, amounts to less than 5% at 1700 A, it is apparent that one would be better off using a single plate of suprasil as a reference rather than an empty cell. This plate should have a thickness equal to the sum of the two sample cell windows. In studying a solution one should run a spectrum of the solvent and then one of the solution relative to the silica plate. No difficulty should be experienced in estimating the actual stray light level, since the water spectrum will go through a minimum and gradually rise as the wavelength is shortened. Any transmittance reading at wavelengths shorter than the minimum is due to stray light, and in fact is a direct quantitative measure of stray light. This effect is evident in the extreme left end of Figure 7.

In handling gases the usual precautions of using vacuum tight cells must be observed. Leakage of air into the cell can usually be detected from the oxygen absorption bands in the 1750-1850 A regions. If a mercury manometer is used to indicate pressure, the atomic absorption lines of mercury at 1849 and 2536 A will be observed. Vapors of pump oil can be troublesome with long sample paths. When using very short path cells of small volume, one may experience considerable difficulty in obtaining known pressures of sample gas due to absorption on cell walls. Under these conditions it may be advantageous to use a flow through cell and continually circulate gas at a constant pressure through the cells.

Finally caution must be exercised with regard to sample purity. It is not unusual to find that an impurity may possess an absorptivity 10 to 1000 times greater than the pure samples in question; hence will cause trouble even at very low concentration. Furthermore, the energetic far ultraviolet light may decompose the sample. This factor is of particular significance, when the sample is placed in the entrance optics or when the sample floods the entire monochromator. Sample decomposition has not been detected in working with the far uv DK instruments. In this instrument the level of light intensity passing through the sample is very low since the sample is in the exit optics.

Analytical Applications

The two major factors of concern in selecting a spectral region for analysis are specificity and sensitivity. On both of these counts the far ultraviolet region has much to offer for the study of gases. With the exception of the rare gases, hydrogen, nitrogen, and saturated hydrocarbons, virtually all of the inorganic gases and organic vapors absorb in the 1700-2200 A region. The absorption spectra are often very detailed. In the case of liquids the specificity of far ultraviolet spectra is about the same as that for the near ultraviolet liquid spectra.

Most of the papers in the literature have dealt with some interpretation of molecular structure. While many of these articles have pointed out analytical applications, few actually document an analysis. The few that have been reported are outlined here.

TABLE III. REFERENCES TO FAR ULTRAVIOLET SPECTRA OF ORGANIC COMPOUNDS

Formula	*Name*	*State*	*λ, A*	*Reference*
C	Carbon	Vapor	1000-2000	171
CHO_2Na	Sodium formate	Solution	1800-3000	99
$CHClF_2$	Chlorodifluoromethane	Vapor	1150-1750	174
$CHCl_3$	Chloroform	Solution	1700-2100	248
CHF_3	Fluoroform	Vapor	770-1430	176
CHN	Hydrogen cyanide	Vapor	1000-2000	145,247
CH_2O	Formaldehyde	Vapor	1540-2000	43
CH_2O_2	Formic acid	Solution	1800-3000	99
CH_2F_2	Methylene fluoride	Vapor	535-2200	206
CH_3 $(CD)_3$	Methyl radical	Vapor	1300-2200	245
CH_3F	Methyl fluoride	Vapor	770-1430	176
CH_3I	Methyl iodide	Vapor	1650-2200	62,6a
CH_4	Methane	Vapor	350-1600	32,178
		Vapor	1050-1600	115,150,220
		Vapor	1400-2000	225
CH_4O	Methanol	Vapor	500-1300	124
		Vapor	1670-2000	65
CH_4ON_2	Urea	Solution	1800-3000	99
CH_4S	Methanethiol	Vapor	1200-2000	148
CH_5N	Methylamine	Vapor	1590-2560	196
		Vapor	1986-2525	69
CCl_2F_2	Freon	Vapor	1100-1950	174
CCl_4	Carbon tetrachloride	Solution	1700-2000	248
CF_4	Carbon tetrafluoride	Vapor	1334-2000	115
CO	Carbon monoxide	Vapor	374-1306	177
		Vapor	884	182
		Vapor	1050-2500	103,186, 194,220
		Vapor	1230-1750	244
CO_2	Carbon dioxide	Vapor	374-1306	177
		Vapor	1050-1800	74,220
		Vapor	1215	140
		Vapor	1400-2000	225
		Solution	1950-2400	68
CS_2	Carbon disulfide	Vapor	856	195
		Vapor	1000-3000	143
		Solution	1700-2200	248
C_2HCl_3	Trichloroethylene	Vapor		209
C_2H_2	Acetylene	Vapor	780-1850	121
		Vapor	1000-2000	114,145,232
		Vapor	1970-2470	76
		Vapor	2200	77
C_2H_2O	Ketene	Vapor	1300-1830	151
$C_2H_2O_2$	Glyoxal	Vapor	1300-2800	212
$C_2H_2O_4$	Oxalic acid	Solution	1800-3000	99
$C_2H_2Cl_2$	1,2-Dichloroethylene	Vapor		209
$C_2H_2Cl_2$	1,1-Dichloroethylene	Vapor	1100-2100	197
$C_2H_3O_2Na$	Sodium acetate	Solution	1800-3000	99
C_2H_3Cl	Vinyl chloride	Vapor		209
C_2H_4	Ethylene	Vapor	1060-2000	237
		Vapor	1300-1500	229
		Vapor	1400-2000	63,225
		Vapor	1500-2050	88,133,226
C_2H_4O	Ethylene oxide	Vapor	600-4000	100
		Vapor	1100-1800	104
		Vapor	1540-2000	43
C_2H_4O	Acetaldehyde	Vapor	1520-2000	97,213
$C_2H_4O_2$	Acetic acid	Solution	1700-2450	99,128, 165,248
C_2H_5ON	Acetamide	Solution	1800-3000	99
$C_2H_5O_2N$	Glycine	Solution	1800-3000	99,248
C_2H_5Br	Ethyl bromide	Vapor & Solid	1650-2400	6a
C_2H_5I	Ethyl iodide	Vapor & Solid	1652-2400	6a
C_2H_6	Ethane	Vapor	1550	90,150
C_2H_6O	Dimethyl ether	Vapor	1600-1950	66
C_2H_6O	Ethanol	Vapor	500-1300	124
		Vapor	1670-2000	65
		Liquid	1760-2100	90
C_2H_7N	Dimethylamine	Vapor	1590-2560	196
		Solution	1700-2400	248
C_2H_7N	Ethylamine	Vapor	1590-2560	196
$C_2O_4Na_2$	Sodium oxalate	Solution	1800-3000	99
C_2Cl_4	Tetrachloroethylene	Vapor		209
$C_2Cl_2F_4$	Tetrafluoro-dichloroethane	Vapor	1100-1950	174
C_2N_2	Cyanogen	Vapor	1000-2000	145
C_3H_3N	Acrylonitrile	Solution	1700-2200	248
C_3H_4	Allene	Vapor	1200-2030	180
C_3H_4	Methylacetylene	Vapor	1000-2000	145

Table III. References to Far Ultraviolet Spectra of Organic Compounds—*(Continued)*

Formula	*Name*	*State*	λ, *A*	*Reference*
C_3H_4O	Acrolein	Vapor	-1900	210
C_3H_5Cl	Chlorocyclopropane	Vapor	1670-1920	39
C_3H_6	Propene	Vapor	1680-1920	88
C_3H_6	Cyclopropane	Vapor	600-2200	205
C_3H_6O	Acetone	Vapor	1500-2000	71,97
		Solution	1720-2000	128,248
C_3H_6O	Trimethylene oxide	Vapor	1540-2000	43
$C_3H_6O_3$	Dimethyl carbonate	Solution	1800-3000	99
C_3H_7ON	Propionamide	Solution	1750-2000	200
$C_3H_7O_2N$	Urethane	Solution	1800-3000	99
$C_3H_7O_2N$	Alanine	Solution	1800-3000	99
C_3H_8O	1-Propanol	Vapor	500-1300	124
		Vapor	1670-2000	65
		Solution	1730-1980	128
		Solution	1540-1820	248
C_3H_8O	2-Propanol	Vapor	1670-2000	65
C_3H_9N	Trimethylamine	Vapor	1590-2560	196
		Solution	1700-2500	248
$C_3H_{12}N_3B_3$	B-Trimethylborazole N-Trimethylborazole	Solution	1700-2300	153,248
C_4H_2	Diacetylene	Vapor	1000-2000	145
$C_4H_2N_2Cl_2$	2,4-Dichloropyrimidine	Solution	1700-3000	248
C_4H_4O	Furan	Vapor	1050-2150	221
		Solution	1700-2300	248
$C_4H_4ON_2$	Methylpyridazone	Solution	1800-3000	248
$C_4H_4O_4Na$	Sodium succinate	Solution	1800-3000	99
$C_4H_4N_2$	Pyridazine	Solution	1720-3100	248
$C_4H_4N_2$	Pyrimidine	Solution	1720-3100	248
$C_4H_4N_2$	Pyrazine	Solution	1720-3100	248
C_4H_4S	Thiophene	Solution	1700-2500	248
$C_4H_5O_2N$	Succinimide	Solution	1750-2000	200
C_4H_5N	Pyrrole	Solution	1700-2400	248
C_4H_6	1-Butyne	Vapor	1680-1900	88
C_4H_6	1,2-Butadiene	Vapor	1680-2100	88,248
C_4H_6	1,3-Butadiene	Vapor	1650-2200	66,88
		Solution	1700-2400	248
C_4H_6	Cyclobutene	Vapor	1560-2500	102
C_4H_6O	Crotonaldehyde	Vapor	-1900	210
C_4H_6O	Divinyl ether	Vapor	1600-2500	64,66
$C_4H_6O_2$	Diacetyl	Solution	1700-2200	248
$C_4H_6O_2$	Crotonic acid	Solution	1700-2400	165,248
$C_4H_6O_2N_2$	Glycine anhydride	Solution	1780-2300	248
$C_4H_6O_3$	Acetic anhydride	Solution	1800-3000	99
$C_4H_6O_3N_2$	Glycine anhydride	Solution	1800-	60
$C_4H_6O_4$	Dimethyl oxalate	Solution	1800-3000	99
$C_4H_6O_4$	Succinic acid	Solution	1800-3000	99
C_4H_7	Methylcyclopropane	Vapor	600-2200	205
C_4H_8	1-Butene	Vapor	1680-1950	88
C_4H_8	2-Butene	Vapor	1560-2220	53,88
C_4H_8	2-Methylpropene	Vapor	1680-2100	88
C_4H_8O	Methyl ethyl ketone	Solution	1740-2500	128
C_4H_8O	Tetrahydrofuran	Solution	1800-2000	248
$C_4H_8O_2$	Ethyl acetate	Solution	1800-3000	99
$C_4H_8O_2$	Butyric acid	Solution	1800-3000	99
$C_4H_8O_2$	Dioxane	Solution	1820-2000	248
C_4H_9ON	Isobutyramide	Solution	1750-2000	200
C_4H_9Cl	*n*-Butyl chloride	Solution	1700-1900	248
$C_4H_{10}O$	*n*-Butanol	Vapor	500-1300	124
		Solution	1730-2000	128
$C_4H_{10}O$	*sec.* Butyl alcohol	Solution	1730-2270	128
$C_4H_{10}O$	*tert.* Butyl alcohol	Solution	1815-1980	128
$C_4H_{10}O$	Diethyl ether	Vapor	1600-1950	66
		Liquid	1980	90
$C_4H_{10}O_2$	Butyric acid	Solution	1900-2340	128
$C_4H_{10}O_2FP$	Isopropyl methyl phosphonofluoridate	Vapor	1150-1650	174
$C_4H_{11}N$	Diethylamine	Vapor	1590-2560	196
		Solution	1800-3000	99
$C_4H_{11}N$	Isobutylamine	Solution	1700-2300	248
C_4F_8	Perfluorocyclobutane	Liquid	1860	90
$C_5H_4O_2$	Furfuraldehyde	Vapor	1600-2600	211
C_5H_5N	Pyridine	Vapor	1100-2200	147
C_5H_6	Methylcyclobutene	Vapor	1560-2500	102
C_5H_6	Cyclopentadiene	Vapor	1760-2000	175
		Solution	1780-2500	248
$C_5H_6N_2$	3-methylpyridazine	Solution	1800-3300	248
$C_5H_7O_2N$	Glutarimide	Solution	1750-2000	200
$C_5H_7O_2N$	Methylsuccinimide	Solution	1750-2000	200
C_5H_8	1,2-Pentadiene	Vapor	1680-2100	88
C_5H_8	1,3-Pentadiene	Vapor	1680-2400	78,88
		Solution	1700-2500	248
C_5H_8	1,4-Pentadiene	Vapor	1650-2000	66,88
C_5H_8	2,3-Pentadiene	Vapor	1680-2120	88
C_5H_8	2-Methyl-1,3-butadiene	Vapor	1680-2280	78,88
C_5H_8	Cyclopentene	Vapor	1680-2100	88
C_5H_8	1-Methylcyclobutene	Vapor	1560-2500	102
C_5H_8O	2,3-Dihydropyrane	Solution	1700-2200	133,248
C_5H_9	2, Methyl-1-butene	Vapor	1560-2500	102
$C_5H_9O_2N$	Proline	Solution	1800-3000	99
C_5H_{10}	Cyclopentane	Liquid	1725	90
C_5H_{10}	1-Pentene	Vapor	1540-2200	170
		Vapor	1680-1950	88
C_5H_{10}	3 Methyl-1-butene	Vapor	1540-2200	170
		Vapor	1680-1950	88
C_5H_{10}	2-Pentene	Vapor	1540-2220	170
C_5H_{10}	2-Methyl-2-butene	Vapor	1690-2100	88
		Solution	1690-2100	248
$C_5H_{10}O$	Diethyl ketone	Solution	1780-2100	128,248
$C_5H_{10}O$	2-Pentanone	Solution	1910-2300	128
$C_5H_{10}O$	*iso*Valeraldehyde	Solution	1860-2300	128
$C_5H_{11}O_2N$	Valine	Solution	1800-3000	99
C_5H_{12}	*n*-Pentane	Liquid	1710	90
C_5H_{12}	*iso*Pentane	Liquid	1700-	137
$C_5H_{12}O$	*n*-Amyl alcohol	Solution	1730-2350	128
$C_5H_{12}O$	Diethyl carbinol	Solution	1760-2000	128
C_6H_2	Hexatriene	Vapor	1200-2700	146
$C_6H_3Cl_3$	Trichlorobenzene	Solution	1800-2900	248
$C_6H_4Cl_2$	*o*-Dichlorobenzene	Vapor	1100-2200	147
		Solution	1700-2300	248
C_6H_5Br	Bromobenzene	Vapor	1100-2200	147
		Solution	1700-2400	248
C_6H_5Cl	Chlorobenzene	Vapor	1100-2200	147
		Solution	1700-2800	248
C_6H_5F	Fluorobenzene	Vapor	1200-2200	61
		Solution	1700-2700	248
C_6H_5I	Iodobenzene	Vapor	1100-2200	147
		Solution	1700-2300	248
$C_6H_5O_2N$	Nitrobenzene	Solution	1730-2500	248
C_6H_6	Benzene	Vapor	400-1300	20
		Vapor	1100-2200	147,61
		Vapor	1300-1850	227,228
		Vapor	1450-2080	63
		Vapor	1680-2100	88
		Vapor	1850-2100	138
		Vapor	1900-2030	158
		Solution	1700-2300	130,132,248
		Solid	1900-2030	158
C_6H_6	Divinylacetylene	Vapor	1200-2700	146
C_6H_6	Di(Methylacetylene)	Vapor	1000-2000	145
C_6H_6O	Phenol	Vapor	1200-2200	61
		Solution	1750-2900	248
C_6H_6S	Thiophenol	Solution	1740-2400	248
$C_6H_6O_2$	Hydroquinone	Solution	1750-2400	248
C_6H_6NCl	*o*-Chloroaniline	Solution	1700-3000	248
C_6H_7N	Aniline	Solution	1700-2400	248
$C_6H_9O_2N$	Dimethylsuccinimide	Solution	1750-2000	200
C_6H_{10}	1,5-Hexadiene	Vapor	1680-1950	88
C_6H_{10}	4-Methylpentadiene	Solution	1700-2200	248
C_6H_{10}	2,3-Dimethyl-1,3-butadiene	Vapor	1680-2320	88
		Solution	1700-2300	248
C_6H_{10}	Cyclohexene	Vapor	1680-2100	88
		Solution	1700-2200	133,248
$C_6H_{10}O$	Mesityl oxide	Vapor	-1900	210
C_6H_{11}	Methylcyclopentane	Liquid	1750	90
C_6H_{12}	1-Hexene	Vapor	1670-2500	54,88
		Solution	1680-1950	88,248
C_6H_{12}	2-Hexene	Solution	1720-2100	88
C_6H_{12}	3-Hexene	Vapor	1670-2500	54
C_6H_{12}	Cyclohexane	Liquid	1765	90
C_6H_{12}	2-Methyl-1-pentene	Vapor	1680-1950	88,170
C_6H_{12}	3-Methyl-1-pentene	Vapor	1540-2200	88
C_6H_{12}	4-Methyl-1-pentene	Vapor	1690-1950	88
C_6H_{12}	2,3 Dimethyl-1-butene	Vapor	1670-2500	54
C_6H_{12}	3,3 Dimethyl-1-butene	Vapor	1690-1950	88
C_6H_{12}	2,3 Dimethyl-2-butene	Vapor	1670-2500	54,88
		Solution	1680-2350	88,248
C_6H_{12}	2-Methyl-2-pentene	Vapor	1690-2100	88
		Solution	1690-2100	88
C_6H_{12}	3-Methyl-2-pentene	Vapor	1690-2200	88
C_6H_{12}	2-Ethyl-1-butene	Vapor	1680-2100	88

TABLE III. REFERENCES TO FAR ULTRAVIOLET SPECTRA OF ORGANIC COMPOUNDS—*(Continued)*

Formula	*Name*	*State*	*λ, A*	*Reference*
$C_6H_{12}O_4N_2S_2$	Cystine	Solution	1800-3000	99,248
$C_6H_{13}O_2N$	Leucine	Solution	1800-3000	99
C_6H_{14}	*n*-Hexane	Liquid	1700-7000	128,137,253
C_6H_{14}	3-Methylpentane	Liquid	1800-7000	137
C_6H_{14}	Neohexane	Liquid	1760-	90
C_6Cl_6	Hexachlorobenzene	Solution	1700-3100	248
$C_7H_4F_4$	Fluoro Benzo-Trifluoride	Vapor	1200-2200	61
C_7H_5N	Benzonitrile	Vapor	1100-2300	214
		Solution	1700-2400	248
C_7H_5NO	Phenyl Isocyanate	Vapor	1100-2700	214
$C_7H_5F_3$	Benzotrifluoride	Vapor	1200-2200	61
		Solution	1700-2700	248
C_7H_6O	Benzaldehyde	Vapor	1600-2600	211
		Solution	1700-2600	248
$C_7H_6O_2$	Benzoic acid	Solution	1700-2500	248
$C_7H_7O_2N$	*o*-Aminobenzoic acid	Solution	1700-2600	248
C_7H_7F	Fluorotoluene (*o,m,p*)	Vapor	1200-2200	61
		Solution	1700-2700	248
C_7H_8	Toluene	Vapor	1100-2200	147,61
		Vapor	1850-2100	138
		Solution	1700-2300	88,130, 132,248
C_7H_9O	Cresol	Solution	1700-2300	248
C_7H_9ON	Anisidine	Solution	1700-2500	248
C_7H_9N	Methylaniline	Solution	1700-3000	248
C_7H_{10}	Bicyclo(2,2,1)heptene-2	Vapor	1540-2200	175
C_7H_{12}	Bicyclo(2,2,1)heptane	Vapor	1540-2200	175
$C_7H_{12}O$	Methylamyl ketone	Solution	1850-1950	128
$C_7H_{13}O_2N$	Piperidine acetate	Solution	1800-3000	99
C_7H_{14}	Methylcyclohexane	Liquid	1700-1900	137
C_7H_{16}	*n*-Heptane	Liquid	1700-2300	88,90,137
C_7H_{16}	3-Methylhexane	Liquid	1730	90
C_7H_{16}	Methylcyclohexane	Liquid	1790	90
C_7H_{16}	2,3 Dimethylpentane	Liquid	1790	90
C_7H_{16}	2,2,3 Trimethylbutane	Liquid	1780	90
C_7F_8	Perfluorotoluene	Solution	1700-2700	248
C_7F_{16}	*n*-Perfluoroheptane	Liquid	1800-	42,90
C_8H_6	Phenyl acetylene	Vapor	1100-2400	214
		Solution	1700-2500	248
C_8H_6O	Benzofuran	Solution	1720-2800	248
C_8H_6S	Thionaphthene	Solution	1720-2800	248
C_8H_7N	Indole	Solution	1720-2800	248
C_8H_8	Styrene	Vapor	1100-2600	214
		Solution	1720-2800	248
$C_8H_8O_2$	Toluic acid	Solution	1700-2500	248
$C_8H_{11}O_2N$	Hexahydrophthalimide	Solution	1750-2000	200
		Vapor	1200-2200	61
C_8H_{10}	Ethylbenzene	Solution	1700-2250	61,130
C_8H_{10}	Xylene (*o,m,p*)	Vapor	1100-2200	61,147
		Vapor	1850-2100	138
		Solution	1700-2300	88,130, 132,248
$C_8H_{11}N$	Dimethylaniline	Solution	1700-3000	248
$C_8H_{13}O_2N$	Tetramethylsuccinimide	Solution	1750-2000	200
C_8H_{14}	1-Octyne	Solution	1700-2200	133,248
C_8H_{14}	2-Octyne	Solution	1700-2200	133,248
C_8H_{16}	1-Octene	Solution	1700-2200	90,133,248
C_8H_{16}	2-Octene	Solution	1700-2200	90,133,248
C_8H_{16}	3-Octene	Solution	1700-2400	128,165
$C_8H_{16}O_2$	Caprylic acid	Solution	1700-2400	128,165
C_8H_{18}	*iso*-Octane	Liquid	1700-	90,128
C_8H_{18}	2,2,3 Trimethylpentane	Liquid	1790-	90
$C_8H_{18}O$	Di-*n*-butyl ether	Solution	1730-1920	128
$C_8H_{18}O$	*sec.* Octyl alcohol	Solution	1730-2000	128
C_8F_{18}	*n*-Perfluorooctane	Liquid	1592	91
C_9H_{10}	α-Methylstyrene	Vapor	1100-2500	214
$C_9H_{11}O_2N$	Phenylalanine	Solution	1800-2200	248
$C_9H_{11}O_3N$	Tyrosine	Solution	1800-2300	248
C_9H_{12}	Cumene	Vapor	1200-2200	61
C_9H_{12}	Mesitylene	Solution	1700-2300	88,153,248
C_9H_{12}	1-Methyl-2-ethylbenzene	Solution	1730-2300	88
C_9H_{20}	2,2,3,3-Tetramethyl-pentane	Liquid	1795-	90
C_9F_{20}	*n*-Perfluorononane	Liquid	1830	90
$C_{10}H_8$	Naphthalene	Vapor	1200-2200	61
		Solution	1700-4000	88,92, 108,248

TABLE III. REFERENCES TO FAR ULTRAVIOLET SPECTRA OF ORGANIC COMPOUNDS—*(Continued)*

Formula	*Name*	*State*	*λ, A*	*Reference*
$C_{10}H_8$	Azulene	Solution	1600-7000	108,248
$C_{10}H_8N_2$	Dipyridyl	Solution	1700-3000	248
$C_{10}H_{12}$	Tetralin	Solution	1730-2300	88
$C_{10}H_{14}$	*n*-Butylbenzene	Solution	1700-2300	132
$C_{10}H_{14}$	*t*-Butylbenzene	Solution	1700-2200	248
$C_{10}H_{14}$	1,2,3,5-Tetramethyl-benzene	Solution	1720-2300	88
$C_{10}H_{22}$	*n*-Decane	Liquid	1725	90
$C_{11}H_{10}$	2-Methylnaphthalene	Solution	1720-2300	88
		Vapor	1200-2200	61
$C_{11}H_{12}O_2N_2$	Tryptophane	Solution	1800-2300	248
$C_{12}H_9N$	Carbazole	Solution	1700-2400	248
$C_{12}H_9I$	Iododiphenyl	Solution	1700-2400	248
$C_{12}H_{10}$	Diphenyl	Solution	1720-2900	248
$C_{12}H_{10}$	Acenapthene	Solution	1700-3000	92,248
$C_{12}H_{10}N_2$	Azobenzene	Solution	1700-3000	248
$C_{12}H_{26}$	*n*-Dodecane	Liquid	1730	90
$C_{13}H_{10}$	Fluorene	Solution	1700-3000	248
$C_{13}H_{10}O$	Benzophenone	Solution	1730-2300	248
$C_{13}H_{12}$	Diphenylmethane	Solution	1700-2700	248
$C_{14}H_{10}$	Anthracene	Vapor	1520-2800	249
		Solution	1700-4000	88,92,248
$C_{14}H_{10}$	Phenanthrene	Solution	1700-4000	88,92,248
$C_{14}H_{14}$	Dibenzyl	Solution	1720-2300	248
$C_{14}H_{28}O_2$	Myristic acid	Solution	1700-2400	128,165,248
$C_{16}H_{10}$	Fluoranthene	Solution	1700-3000	248
$C_{16}H_{10}$	Pyrene	Solution	1700-3000	248
$C_{16}H_{26}$	*n*-Decylbenzene	Solution	1720-2150	88
$C_{16}H_{32}O_2$	Ethyl myristate	Solution	1720-2400	165
$C_{17}H_{11}$	1,2-Benzanthrene	Solution	1700-4000	92
$C_{17}H_{32}O_2$	2-Heptadecenoic Acid	Solution	1720-2400	165
$C_{18}H_{12}$	1,2-Benzanthracene	Solution	1720-2100	88,248
$C_{18}H_{12}$	Chrysene	Solution	1720-4000	88,92,248
$C_{18}H_{12}$	Naphthacene	Solution	1720-3000	248
$C_{18}H_{15}N$	Triphenylamine	Solution	1700-2500	248
$C_{18}H_{16}$	Diphenylbenzene	Solution	1700-3000	248
$C_{18}H_{30}$	Hexaethylbenzene	Solution	1700-2800	248
$C_{18}H_{30}O_2$	Linolenic acid	Solution	1700-2400	165,248
$C_{18}H_{30}O_2$	*pseudo*-Eleostearic acid	Solution	1700-2400	165
$C_{18}H_{32}O_2$	Linoleic acid	Solution	1700-2400	165,248
$C_{18}H_{34}O_2$	Oleic acid	Solution	1700-2400	165,248
$C_{18}H_{34}O_2$	Elaidic acid	Solution	1700-2400	165
$C_{20}H_{14}$	Dinaphthyl	Solution	1720-2300	88
$C_{20}H_{34}O_2$	Ethyl linolenate	Solution	1700-2400	165
$C_{21}H_{42}O_2$	Methyl arachidonate	Solution	1700-2400	165,248
C_nF_{2n}	Teflon	Film	1700-	22,90
	Celluloid	Film	300-2000	122
	Cellulose acetate	Film	80-260	183
	Steroids	Solution	1750-2100	201,248,252
	Terpenoids	Solution	1750-2100	201

Gunther and co-workers used the edge of the far ultraviolet for the analysis of ammonia in nitrogen and in air *(243)*. Figure 5 shows the spectrum of ammonia. Gunther used the 2043 A band and specified a detectability of 7 ppm of ammonia in air or nitrogen using a 10 cm cell. Obviously any one of several bands could be used. The bands at 1936 and 1972 A would allow an even more sensitive analysis for ammonia in nitrogen. However the absorption of oxygen and water vapor would interfere with the use of these bands for the analysis of ammonia in air.

The possibility of using far ultraviolet radiation for the analysis of water vapor in the air was recognized by Bologna *et al (240)*. They purported to use the Lyman α line as a source. Theoretically this radiation would allow excellent sensitivity and good discrimination. Water vapor has an absorptivity of „387 cm^{-1} while oxygen has an absorptivity of 0.3 cm^{-1} at this wavelength (1216 A). Unfortunately these workers miscalculated the necessary optical path length.

The effects of varying concentration of water vapor in the atmosphere are evident on scanning with the far uv

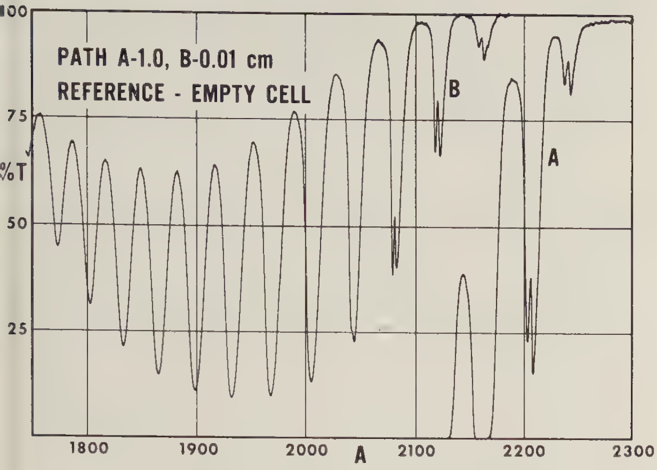

Fig. 5. Spectrum of Ammonia Vapor

DK spectrophotometer in the region from 1800-1900 A. Water vapor has a non-discrete spectra while oxygen absorbs very discretely in this region (see Figure 5 of the first paper in this series, *(89a)*.) However the absorptivity of water vapor is about 10 times that of the oxygen minima.

Carbonyl compounds have characteristic absorption spectra in the 1700-2000 A region. All of these compounds have a strong absorption band at about 1940 A. This band has been applied to the analysis of acetone in acetylene *(89)*.

Jones and Taylor have studied the spectra of a large number of unsaturated and aromatic compounds *(88)*. They call attention to the analytical possibility of the 1700-2000 A region but do not report results on specific mixtures. It is apparent from their spectra that one could analyze for any unsaturate in a non-absorbing matrix with a sensitivity of a few ppm. However, the analysis of one olefin in the presence of another olefin would be possible in only a few cases. The aromatics are much more selective.

Fatty acid solutions have been studied to about 1750 A *(165)*. The absorptivities of these acids have been correlated with the number of double bonds in these acids.

Table II lists a number of publications on the spectra of metallic vapors. None of these papers were concerned with analysis, but the information could be put to this use. The field of atomic absorption spectroscopy has received considerable attention recently, although the author is not aware of its extention into the far ultraviolet for

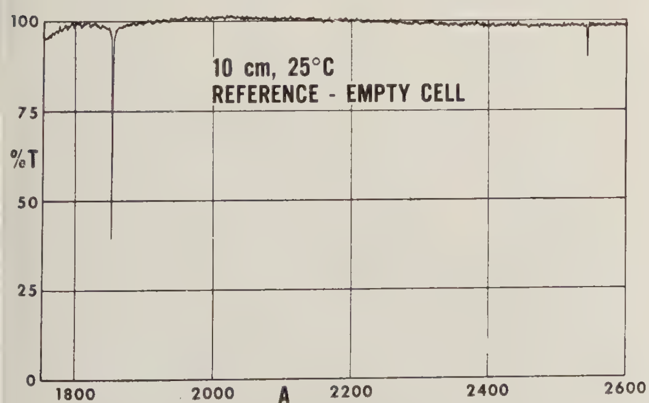

Fig. 6. Spectrum of Mercury Vapor

analytical purposes. However there is reason to suppose that such studies would be possible. Of course the use of a flame to volatize and contain the sample vapor has limitations in the far ultraviolet because of the absorption of oxygen and water vapor in the flame.

One of the simplest examples of atomic absorption spectroscopy is in the analysis of mercury vapor. The 2536 A resonance absorption line of mercury has long been used to determine the concentration of mercury vapor in the air. The 1849 A line of mercury possesses even greater absorptivity and may be used to extend the sensitivity of this method. Figure 6 shows the transmittance spectrum of 10 cm of mercury vapor at room temperature. Of course these absorption bands possess a narrower half band width than the effective band width pased by the monochromator so that the apparent absorptivity is a function of mechanical slit width. However, the DK spectrophotometer has adequate resolution to show the self reversal effect at 1849 A caused by mercury vapor in the Beckman 30 watt mercury lamp. The two resonance lines of mercury provide a very convenient tool for wavelength calibration. A small drop of mercury need only be placed in a 1 or 10 cm cell followed by a purge of the cell with nitrogen.

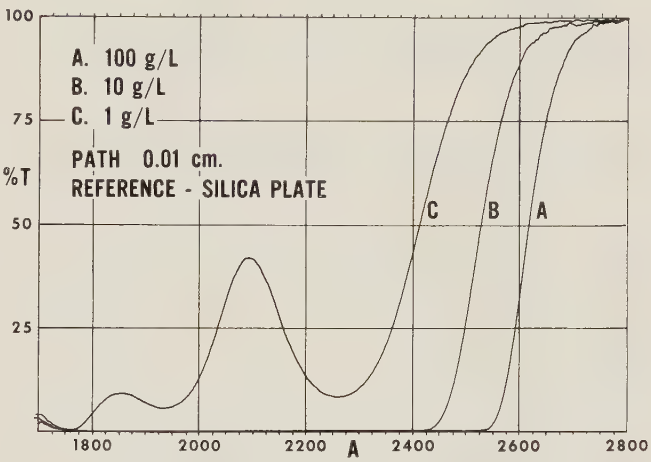

Fig. 7. Spectra of Aqueous Potassium Iodide Solutions

The analysis of inorganic salts in solution is also possible by far ultraviolet spectroscopy. Figure 7 shows the spectra of potassium iodide solutions at several concentrations. Sodium iodide possess an almost identical spectrum. The alkaline bromides show an absorption maximum at 1900 A. Ceric salts have been observed to possess an intense maximum at 2000 A.

Literature Cited

(1) A. A. Aboud, J. P. Curtis, R. Mercure, and W. A. Rense, *Oxygen Gas Continuous Absorption in the Extreme Ultraviolet*, J. Opt. Soc. Am. **45**, 767-8 (1955)

(2) N. Astoin, A. J. Gilles, and B. Vodar, *Absorption of Water Vapour in the Extreme Ultraviolet*, Compt. rend. **237**, 558-60 (1953)

(3) N. Astoin and B. Vodar, *Thin Transparent Films in the Far Ultraviolet*, J. phys. radium **14**, 424-5 (1953)

(4) N. Astoin and J. Granier, *On the Absorption Spectrum of N_2O in the Extreme Ultraviolet*, Compt. rend. **241**, 1736-8 (1955)

(5) N. Astoin, *On the Absorption Spectrum of the Vapour of Water and Heavy Water in the Extreme Ultraviolet,* IBID. **242**, 2327-9 (1956)

(6) N. Astoin and J. Granier, *The Vacuum Ultraviolet Absorption Spectrum of Nitrogen,* IBID. **244**, 1350-3 (1957)

(6a) N. Astoin, J. Granier, and M. Cordier, *Absorption Spectra in the Far Ultraviolet of Gaseous and Solid Methyl and Ethyl Iodides and Ethyl Bromide,* J. PHYS. RADIUM, **19**, 507-508 (1958)

(7) N. N. Axelrod and M. P. Givens, *Absorption by Gaseous Helium in the Extreme Ultraviolet,* PHYS. REV. **115**, 97 (1959)

(8) R. F. Barrow, C. Drummond, and H. C. Rowlinson, *The Absorption Spectrum of SnS Vapour in the Ultraviolet and Schumann Regions,* PROC. PHYS. SOC. (LONDON) **A66**, 885-8 (1953)

(9) R. F. Barrow and H. C. Rowlinson, *The Absorption Spectra of Gaseous SiO, GeO, SnO, SnS, and AlF in the Schumann Region,* J. PHYS. RADIUM **15**, 499-500 (1954)

(10) R. F. Barrow and H. C. Rowlinson, *The Absorption Spectra of the Gaseous Monoxides of Silicon, Germanium and Tin in the Schumann Region,* PROC. ROY. SOC. (LONDON) **A224**, 374-88 (1954)

(11) R. F. Barrow and H. C. Rowlinson, *The Absorption Spectrum of Gaseous Aluminum Monofluoride in the Schumann Region,* IBID. **A224**, 134-40 (1954)

(12) R. F. Barrow and E. Miescher, *Fine Structure Analysis of NO Absorption Bands in the Schumann Region,* PROC. PHYS. SOC. (LONDON) **A70**, 219-22 (1957)

(13) R. Bauple, A. Gilles, J. Romand, and B. Vodar, *Absorption Spectra of Samples of Quartz and Corundum in Ultraviolet. Electric and Thermic Treatment of Quartz,* J. OPT. SOC. AM. **40**, 788-9 (1950)

(14) N. S. Bayliss and J. V. Sullivan, *Vacuum Ultraviolet Absorption Spectra of Iodine and Bromine,* J. CHEM. PHYS. **22**, 1615-16 (1954)

(15) G. W. Bethke, *Oscillator Strengths in the Far Ultraviolet. I. Nitric Oxide,* IBID. **31**, 662-68 (1959)

(16) G. W. Bethke, *Oscillator Strengths in the Far Ultraviolet. II. Oxygen Schumann-Runge Bands,* IBID. **31**, 669-73 (1959)

(17) J. C. Boyce, *Spectroscopy in the Vacuum Ultraviolet,* REV. MOD. PHYS. **13**, 1-57 (1941)

(18) P. Brix and G. Herzberg, *Fine Structure of the Schumann-Runge Bands Near the Convergence Limit and the Dissociation Energy of the Oxygen Molecule,* CAN. J. PHYS. **32**, 110-135 (1954)

(19) P. H. Brodersen and S. Mayo, *BrF Bands in the Schumann Region,* Z. PHYSIK. **143**, 477-8 (1955)

(20) S. M. Bunch, G. R. Cook, M. Ogawa, and A. W. Ehler, *Absorption Coefficients of C_6H_6 and H_2 in the Vacuum Ultraviolet,* J. CHEM. PHYS. **28**, 740-41 (1958)

(21) M. Chretien, *The Band Spectrum of Boron Monofluoride (BF) in the Schumann Region,* HELV. PHYS. ACTA **22**, 588-90 (1949); **23**, 259-87 (1950)

(22) T. A. Chubb and H. Friedman, *Photon Counters for the Far Ultraviolet,* REV. SCI. INSTR. **26**, 493-98 (1955)

(23) T. A. Chubb, *Transmission of Barium Fluoride Crystals in the Ultraviolet,* J. OPT. SOC. AM. **46**, 362-3 (1956)

(24) A. J. Cohen and H. L. Smith, *Anisotropic Color Centers in α-Quartz. II. Germanium-Doped Synthetic Quartz,* J. CHEM. PHYS. **28**, 401-405 (1958)

(25) H. Cordes, *Absorption Spectrum of I_2 in the Vacuum Ultraviolet,* Z. PHYSIK **97**, 603-624 (1935)

(26) J. Curry and G. Herzberg, *On the Ultraviolet Absorption Bands of Oxygen,* ANN. PHYSIK **19**, 800-808 (1934)

(27) J. P. Curtis, *Absorption Coefficients of Air and Nitrogen for the Extreme Ultraviolet,* PHYS. REV. **94**, 908-10 (1954)

(28) E. Darmois, R. Bauple, A. Gilles, and N. Astoin, *Spectral Transparency of Vitreous Silica after the Passage of Electric Current at High Temperature,* COMPT. REND. **230**, 1851-3 (1950)

(29) R. W. Ditchburn and G. V. Marr, *The Continuous Absorption of Light in Magnesium Vapor,* PROC. PHYS. SOC. (LONDON) **A66**, 655-6 (1953)

(30) R. W. Ditchburn, P. J. Jutsum, and G. V. Marr, *The Continuous Absorption of Light in Alkali-Metal Vapors,* PROC. ROY. SOC. (LONDON) **A219** 89-101 (1953)

(31) R. W. Ditchburn and D. W. O. Heddler, *Absorption Cross-Sections in the Vacuum Ultraviolet. I. Continuous Absorption of Oxygen (1800 to 1300 A),* IBID. **A220**, 61-70 (1953)

(32) R. W. Ditchburn, *Absorption Cross-Section in the Vacuum Ultraviolet. III. Methane,* IBID. **A229**, 44-62, (1955)

(33) R. W. Ditchburn, *Optical Instruments for the Vacuum Ultraviolet,* OPTICA ACTA (PARIS) **3**, 74-80 (1956)

(34) R. W. Ditchburn, *Absorption of Ultraviolet Radiation by the Atmospheric Gases,* PROC. ROY. SOC. (LONDON) **A236**, 216-26 (1956)

(35) K. Dressler, *Ultraviolet and Schumann Spectra of the Neutral and Ionized Molecules PO, PS, NS, P_2,* HELV. PHYS. ACTA **28**, 563-90 (1955)

(36) A. B. F. Duncan, *The Ultraviolet Absorption Spectrum of Ammonia,* PHYS. REV. **47**, 822-7 (1935)

(37) A. Duncanson and R. W. Stevenson, *Some Properties of Magnesium Fluoride Crystallized from the Melt,* PROC. PHYS. SOC. (LONDON) **A72**, 1001-1006 (1958)

(38) R. J. Dwyer and H. W. Leighton, *Discoloration of Quartz Windows of an Ultraviolet Source,* REV. SCI. INSTR. **12**, 156-7 (1941)

(39) E. C. Eberlin and L. W. Pickett, *Far Ultraviolet Spectra of Chlorocyclopropane,* J. CHEM. PHYS. **27**, 1439-40 (1957)

(40) A. W. Ehler and G. L. Weissler, *Ultraviolet Absorption of Atomic Nitrogen in its Ionization Continuum,* J. OPT. SOC. AM. **45**, 1035-43 (1955)

(41) H. W. Etzel and D. A. Patterson, *Optical Properties of Alkali Halides Containing Hydroxyl Ions,* PHYS. REV. **112**, 1112-16 (1958)

(42) D. F. Evans, *Perfluoroheptane as a Spectroscopic Solvent,* J. CHEM. PHYS. **23**, 1429-1430 (1955)

(43) G. Fleming, M. M. Anderson, A. J. Harrison, and L. W. Pickett, *Effect of Ring Size on the Far Ultraviolet Absorption and Photolysis of Cyclic Ethers,* IBID. **30**, 351-54 (1959)

(44) M. Foex and A. J. Gilles, *Transparency in the Far Ultraviolet of Quartz Samples Fused in a Solar Furnace in Various Atmospheres,* COMPT. REND. **237**, 1668-70 (1953)

(45) S. Freed, H. L. McMurry, and E. J. Rosenbaum, *Some Properties of White Sapphire,* J. Chem. Phys. **7,** 853 (1939)

(46) V. Garino-Canina, *The Absorption of Ultraviolet in Quartz and Vitreous Silica,* Rev. Opt. **34,** 365-70 (1955)

(47) W. R. S. Garton, *Arc Spectrum of Gallium; New Absorption Lines in the Schumann Region,* Nature **166,** 317-18 (1950)

(48) W. R. S. Garton, *Absorption Spectrum of Indium Vapor in the Schumann Region,* Ibid. **166,** 150 (1950)

(49) W. R. S. Garton, *Absorption Spectrum of Tin Vapor in the Schumann Region,* Ibid. **166,** 690-1 (1950)

(50) W. R. S. Garton and M. W. Feast, *Schumann-Runge Absorption Bands in Heated Oxygen,* Ibid. **165,** 281-2 (1950)

(51) W. R. S. Garton, *Ultraviolet Absorption Spectrum of Tin Vapor in Atmospheres of Helium and Hydrogen,* Proc. Phys. Soc. (London) **A64,** 591-2 (1951)

(52) W. R. S. Garton, *Schumann Region Absorption Spectrum of Copper Vapour,* Ibid. **A65,** 461-2 (1952)

(53) J. T. Gary and L. W. Pickett, *The Far Ultraviolet Absorption Spectra of the Isomeric Butanes,* J. Chem. Phys. **22,** 599-602 (1954)

(54) J. T. Gary and L. W. Pickett, *The Far Ultraviolet Absorption Spectra of Selected Isomeric Hexenes,* Ibid. **22,** 1266-7 (1954)

(55) A. Gilles, R. Bauple, J. Romand, and B. Vodar, *The Far Ultraviolet Absorption Spectra of Some Optical Materials,* Compt. rend. **229,** 876-8 (1949)

(56) A. Gilles, *Absorption at High Temperature of Some Optical Materials in the Schumann Ultraviolet,* J. phys. radium **13,** 247 (1952)

(57) J. Granier-Mayence and J. Romand, *Additional Study on the Absorption Spectrum of Solid Nitrous Oxide in the Schumann Region,* Ibid. **14,** 428-9 (1953)

(58) J. Granier-Mayence and J. Romand, *Absorption Spectrum of Solid Nitric Oxide Between 2400 and 1600 A,* Compt. rend. **236,** 1148-51 (1953)

(59) J. Granier and N. Astoin, *On the Absorption Spectrum of Nitric Oxide in the Far Ultraviolet,* Ibid. **242,** 1431-3 (1956)

(59a) H. Greiner, *The Validity of Beer's Law for the Absorption of Extreme Ultraviolet Light in Oxygen and Nitrogen,* Z. angew. Phys. **9,** 434-7 (1957)

(59b) J. S. Ham, J. R. Platt, and H. McConnell, *The Ultraviolet Spectra of Benzene-Halogen Complexes and of Iodine in Solution,* J. Chem. Phys. **19,** 1301-4 (1951)

(60) J. S. Ham and J. R. Platt, *Far Ultraviolet Spectra of Peptides,* Ibid. **20,** 335-6 (1952)

(61) V. J. Hammond, W. C. Price, J. P. Teegan, and A. D. Walsh, *The Absorption Spectra of Some Substituted Benzenes and Naphthalenes in the Vacuum Ultraviolet,* Disc. Faraday Soc. **9,** 53-60 (1950)

(62) V. J. Hammond and W. C. Price, *A Photoelectric Spectrophotometer for the Vacuum Ultraviolet,* J. Sci. Instr. **31,** 104-6 (1954)

(63) V. J. Hammond and W. C. Price, *Oscillator Strengths of the Vacuum Ultraviolet Absorption Bands of Benzenes and Ethylene,* Trans. Faraday Soc. **51,** 605-10 (1955)

(64) A. J. Harrison, C. L. Gaddis, and E. M. Coffin, *Quantitative Determination of Extinction Coefficients in the Vacuum Ultraviolet: Divinyl Ether,* J. Chem. Phys. **18,** 221-23 (1950)

(65) A. J. Harrison, B. J. Cederholm, and M. A. Terwilliger, *Absorption of Acyclic Oxygen Compounds in the Vacuum Ultraviolet. I. Alcohols,* Ibid. **30,** 355-56 (1959)

(66) A. J. Harrison and D. R. W. Price, *Absorption of Acyclic Oxygen Compounds in the Vacuum Ultraviolet II Ethers,* Ibid. **30,** 357-60 (1959)

(67) P. L. Hartman, J. R. Nelson, and J. G. Siegfried, *Reflection Spectrum and Structure in the Exciton Absorption Peak of NaCl and KCl,* Phys. Rev. **105,** 123-30 (1957)

(68) L. J. Heidt and L. Ekstrom, *Influence of Dissolved Air on Optical Density Measurements of Water Solutions,* J. Am. Chem. Soc. **79,** 1260-61 (1957)

(69) V. Henri and W. Lasareff, *Ultraviolet Absorption Spectrum of Methylamine,* Compt. rend. **200,** 829-30 (1935)

(70) G. Herzberg, A. Lagerqvist, and E. Miescher, *Fine Structure Analysis and Mutual Perturbation of the α and β Bands of the NO Molecule,* Can. J. Phys. **34,** 622-4 (1956)

(71) R. S. Holdsworth and A. B. F. Duncan, *Intensities of Electronic Transitions in Aliphatic Ketones in the Vacuum Ultraviolet,* Chem. Rev. **41,** 311-16 (1947)

(72) J. J. Hopfield, *The Absorption Spectrum of Water Vapor Between 900 and 2000A,* Phys. Rev. **77,** 560-1, (1950)

(73) R. P. Iczkowski and J. L. Margrave, *Absorption Spectrum of Fluorine in the Vacuum Ultraviolet,* J. Chem. Phys. **30,** 403-5 (1959)

(74) E. C. Y. Inn, K. Watanabe, and M. Zelikoff, *Absorption Coefficients of Gases in the Vacuum Ultraviolet. III. CO_2,* Ibid. **21,** 1648-50 (1953)

(75) E. C. Y. Inn, *Vacuum Ultraviolet Spectroscopy,* Spectrochim. Acta **7,** 65-87 (1955)

(76) K. K. Innes, *Analysis of the Near Ultraviolet Absorption Spectrum of Acetylene,* J. Chem. Phys. **22,** 863-76 (1954)

(77) A. Ionesco, *Structure of Ultraviolet Absorption Bands of Acetylene,* Compt. rend. **200,** 817-19 (1935)

(78) L. E. Jacobs and J. R. Platt, *Does Ultraviolet Absorption Intensity Increase in Solution?* J. Chem. Phys. **16,** 1137-45 (1948)

(79) A. Johannin-Gilles, *Variation with Temperature of the Absorption of Water Vapor in the Schumann Ultraviolet,* Compt. rend. **236,** 1345-8 (1953)

(80) A. Johannin-Gilles, *Absorption of Water Vapor in the Schumann Ultraviolet,* Ibid. **236,** 676-78 (1953)

(81) A. Johannin-Gilles and B. Vodar, *On the Absorption Spectrum of Water Vapor in the Schumann Region,* J. phys. radium **15,** 223-4 (1954)

(82) A. Johannin-Gilles, *A New Absorption Band in Lithium Fluoride Irradiated by X-rays,* J. phys. radium **15,** 192 (1954)

(83) A. Johannin-Gilles, *Absorption of the Vapour of Heavy Water in the Schumann Region,* Compt. rend. **240,** 1523-5 (1955)

(84..) A. Johannin-Gilles, N. Astoin, and B. Vodar, *Discussion of the Absorption Spectra of H_2O and D_2O in the Far Ultraviolet*, CAHIERS PHYS. **71-72**, 49-53 (1956)

(85) F. S. Johnson, *Rocket Observations of Atmospheric Ozone*, PROC. TORONTO METEOROL. CONF. **1953**, 17-26 (1954)

(86) J. W. C. Johns and R. F. Barrow, *The Band Spectrum of Silicon Monofluoride SiF*, PROC. PHYS. SOC. **71**, 476-84 (1958)

(87) P. D. Johnson, *Some Optical Properties of MgO in the Vacuum Ultraviolet*, PHYS. REV. **94**, 845-6 (1954)

(88) L. C. Jones, Jr. and L. W. Taylor, *Far Ultraviolet Absorption Spectra of Unsaturated and Aromatic Hydrocarbons*, ANAL. CHEM. **27**, 228-37 (1955)

(89) W. I. Kaye, *Spectroscopy in the Region 175-200 mμ*, AM. SOC. TESTING MATERIALS, SPEC. TECH. PUBL. **No. 269**, 63-72 (1960)

(89a) W. I. Kaye, *Far Ultraviolet Spectroscopy. I. Modification of the Beckman DK Spectrophotometer for Automatic Transmittance Recording in the Region 1700-2000A*, APPLIED SPECTROSCOPY **15**, 89-95 (1961)

(90) H. B. Klevens and J. R. Platt, *Ultraviolet Transmission Limits of Some Liquids and Solids*, J. AM. CHEM. SOC. **69**, 3055-62 (1947)

(91) H. B. Klevens and J. R. Platt, *The Ultimate Liquid Transmision Limit*, J. CHEM. PHYS. **16**, 1168-9 (1948)

(92) H. B. Klevens and J. R. Platt, *Spectral Resemblances of Cata-Condensed Hydrocarbons*, IBID. **17**, 470-81 (1949)

(93) H. P. Knauss and S. S. Ballard, *Rotational Structure of the Schumann-Runge Bands of Oxygen in the Vacuum Region*, PHYS. REV. **48**, 796-99 (1935)

(94) A. R. Knudson and J. E. Kupperian, Jr., *Ultraviolet Transmision of Calcium Fluoride Crystals at Low Temperature*, J. OPT. SOC. AM. **47**, 440-1 (1957)

(95) C. J. Koester and M. P. Givens, *Extreme Vacuum Ultraviolet Absorption Spectra of Silver Chloride and Silver Bromide Films*, PHYS. REV. **106**, 241-3 (1957)

(96) R. Ladenburg and C. C. Van Voorhis, *The Continuous Absorption of Oxygen Between 1750 and 1300 A and its Bearing Upon the Dispersion*, IBID. **43**, 315-21 (1933)

(97) J. S. Lake and A. J. Harrison, *Absorption of Acyclic Oxygen Compounds in the Vacuum Ultraviolet. III. Acetone and Acetaldehyde*, J. CHEM. PHYS. **30**, 361-62, (1959)

(98) J. Lee and A. D. Walsh, *The Vacuum Ultraviolet Absorption Spectra of the Halogen Molecules*, TRANS. FARADAY SOC. **55**, 1282-92 (1959)

(99) H. Ley, and B. Arends, *Absorption Measurements in the Short-Wave Ultraviolet I Carboxylic Acids, Amines and Amino Acids*, Z. PHYSIK. CHEM. **17**, 177-219 (1932)

(100) T. K. Liu and A. B. F. Duncan, *The Absorption Spectrum of Ethylene Oxide in the Vacuum Ultraviolet*, J. CHEM. PHYS. **17**, 241-4 (1949)

(101) T. K. Liu, G. Moe, and A. B. F. Duncan, *The Absorption Spectrum of Sulfur Hexafluoride in the Vacuum Ultraviolet Region*, IBID. **19**, 71-2 (1951)

(102) B. B. Loeffler, E. Eberlin, and L. W. Pickett, *Far Ultraviolet Absorption Spectra of Small Ring Hydrocarbons*, IBID. **28**, 345-47 (1958)

(103) L. H. Long and A. D. Walsh, *Structure of Carbon Monoxide*, TRANS. FARADAY SOC. **43**, 342-51 (1947)

(104) A. Lowrey, III, and K. Watanabe, *Absorption and Ionization Coefficients of Ethylene Oxide*, J. CHEM. PHYS. **28**, 208-10 (1958)

(105) T. Lyman, *The Transparency of the Air Between 1100 and 1300 A*, PHYS. REV. **48**, 149-51 (1935)

(106) R. Maeder and E. Miescher, *Absorption-Band Spectrum of Sulfur in the Schumann Region*, NATURE **161**, 393 (1948)

(107) R. Maeder, *The Absorption Spectrum of S_2 in the Schumann Region*, HELV. PHYS. ACTA **21**, 411-28 (1948)

(108) D. E. Mann, J. R. Platt, and H. B. Klevens, *Spectral Resemblances in Azulene and Naphthalene*, J. CHEM. PHYS. **17**, 481-84 (1949)

(109) F. F. Marmo, *Absorption Coefficients of Nitrogen Oxide in the Vacuum Ultraviolet*, J. OPT. SOC. AM. **43**, 1186-90 (1953)

(110) G. V. Marr, *The Absorption of Light by Thallium Vapour on the Short Wavelength Side of the Series Limit*, PROC. ROY. SOC. (LONDON) **A224**, 83-90 (1954)

(111) G. V. Marr, *A Note on the Absorption of Light by Indium Vapour*, PROC. PHYS. SOC. (LONDON) **A67**, 196-7 (1954)

(112) J. Mayence, J. Romand, and B. Vodar, *The Absorption Spectrum of Gaseous Nitric Oxide in the Schumann Region*, COMPT. REND. **228**, 1799-801 (1949)

(113) E. W. J. Mitchell and E. G. S. Paige, *The Optical Effects of Radiation Induced Atomic Damage in Quartz*, PHIL. MAG. **[8] 1**, 1085-1115 (1956)

(114) G. Moe and A. B. F. Duncan, *Intensities of Electronic Transitions of Acetylene in the Vacuum Ultraviolet*, J. AM. CHEM. SOC. **74**, 3136-40 (1952)

(115) G. Moe and A. B. F. Duncan, *Intensities of Electronic Transitions of Methane and Carbon Tetrafluoride in the Vacuum Ultraviolet*, IBID. **74**, 3140-3 (1952)

(116) K. Mori, *The Absorption Spectrum of Nitrogen Dioxide in the Vacuum Ultraviolet*, SCIENCE OF LIGHT (JAPAN) **3**, 62-9 (1954)

(117) K. Mori, *On the λ 1600-1350 Absorption System of Nitrogen Dioxide and Its Electronic Structure*, IBID. **4**, 130-47 (1955)

(118) A. U. Munck and J. F. Scott, *Ultraviolet Absorption of Oxygen in Organic Solvents*, NATURE **177**, 587 (1956)

(119) T. Nakayama, M. Y. Kitamura, and K. Watanabe, *Ionization Potential and Absorption Coefficients of Nitrogen Dioxide*, J. CHEM. PHYS. **30**, 1180-86 (1959)

(120) J. L. Nickerson, *Some Bands in the Extreme Ultraviolet Spectrum of Helium*, PHYS. REV. **47**, 707-11 (1935)

(121) E. D. Nostrand and A. B. F. Duncan, *Effect of Pressure on Intensity of Some Electronic Transitions in SF_6, C_2H_2 and C_2D_2 Vapours in the Vacuum Ultraviolet Region*, J. AMER. CHEM. SOC. **76**, 3377-9 (1954)

(122) H. M. O'Bryan, *The Absorption and Dispersion of Celluloid Between 300 and 1000 A*, J. OPT. SOC. AM. **22**, 739-48 (1932)

(123) M. Ogawa and G. R. Cook, *Absorption Coefficients of O_3 in the Vacuum Ultraviolet Region*, J. CHEM. PHYS. **28**, 173-4 (1958)

(124) M. Ogawa and G. R. Cook, *Absorption Coefficients of Methyl, Ethyl, n-Propyl and n-Butyl Alcohols,* Ibid. **28**, 747-8 (1958)

(125) R. Onaka, *Study of the $A'\pi \rightarrow X'\Sigma^+$ Bands of $B''F$ with a Vacuum Echelle Spectrograph,* Ibid. **27**, 374-77 (1957)

(126) D. A. Patterson, *Absorption Spectrum of KCl: Tl at Low Temperatures,* Phys. Rev. **112**, 296-7 (1958)

(127) M. K. Phibbs, *Ultraviolet Absorption Spectra of Mercury in Solution,* J. Chem. Phys. **18**, 1679 (1950)

(128) J. R. Platt, I. Rusoff, and H. B. Klevens, *Absorption Spectra of Some Organic Solutions in the Vacuum Ultraviolet,* Ibid. **11**, 535-44 (1943)

(129) J. R. Platt and H. B. Klevens, *Spectroscopy of Organic Molecules in the Vacuum Ultraviolet,* Rev. Mod. Phys. **16**, 182-223 (1944)

(130) J. R. Platt and H. B. Klevens, *Absolute Absorption Intensities of Alkyl Benzenes in the 2250-1700 A Region,* Chem. Rev. **41**, 301-10 (1947)

(131) J. R. Platt, H. B. Klevens, and G. W. Schaeffer, *Absorption Spectrum of Borazole in the Vacuum Ultraviolet,* J. Chem. Phys. **15**, 598-601 (1947)

(132) J. R. Platt and H. B. Klevens, *Further Alkylbenzene Spectra to 1750 A,* Ibid. **16**, 832-4 (1948)

(133) J. R. Platt, H. B. Klevens, and W. C. Price, *Absorption Intensities of Ethylenes and Acetylenes in the Vacuum Ultraviolet,* Ibid. **17**, 466-69 (1949)

(134) Po Lee and G. L. Weissler, *Absolute Absorption of the H_2 Continuum,* Astrophys. J. **115**, 570-1 (1952)

(135) Po Lee, *Photodissociation and Photoionization of Oxygen (O_2) as Inferred from Measured Absorption Coefficients,* J. Opt. Soc. Am. **45**, 703-709 (1955)

(136) P. Popper, *Transmission of Natural and Synthetic Mica in the Ultraviolet,* Nature **168**, 1119-20 (1951)

(137) W. J. Potts, Jr., *Purification of Hydrocarbons for Use as Solvents in Far Ultraviolet Spectroscopy,* J. Chem. Phys. **20**, 809-10 (1952)

(138) W. J. Potts, Jr., *Low Temperature Absorption Spectra of Benzene, Toluene and Para Xylene in the Farther Ultraviolet Region,* Ibid. **23**, 73-9 (1955)

(139) W. M. Powell, Jr., *Photoelectric Measurements of the Absorption of Fused and Crystalline Quartz Between 1633 and 1463 A,* Phys Rev. **46**, 43-46 (1934)

(140) W. M. Preston, *The Origin of Radio Fade-Outs and the Absorption Coefficient of Gases for Light of Wavelength 1215.7 A.* Ibid. **57**, 887-94 (1940)

(141) W. C. Price and G. Collins, *The Far Ultraviolet Absorption Spectrum of Oxygen,* Ibid. **48**, 714-19 (1935)

(142) W. C. Price, *The Absorption Spectra of the Halogen Acids in the Vacuum Ultraviolet,* Proc. Roy. Soc. (London) **A167**, 216-27 (1938)

(143) W. C. Price and D. M. Simpson, *The Absorption Spectra of Sulfur Dioxide and Carbon Disulfide in the Vacuum Ultraviolet,* Ibid. **A165**, 272-91 (1938)

(144) W. C. Price and D. M. Simpson, *Absorption Spectra of Nitrogen Dioxide, Ozone, and Nitrosyl Chloride in the Vacuum Ultraviolet,* Trans. Faraday Soc. **37**, 106-13 (1941)

(145) W. C. Price and A. D. Walsh, *Absorption Spectra of Triple-Bond Molecules in the Vacuum Ultraviolet,* Ibid. **41**, 381-8 (1945)

(146) W. C. Price and A. D. Walsh, *The Absorption Spectra of Hexatriene and Divinyl Acetylene in the Vacuum Ultraviolet,* Proc. Roy. Soc. (London) **A185**, 182-91 (1946)

(147) W. C. Price and A. D. Walsh, *The Absorption Spectra of Benzene Derivatives in the Vacuum Ultraviolet I,* Ibid. **A191**, 22-31 (1947)

(148) W. C. Price, J. P. Teegan, and A. D. Walsh, *Far Ultraviolet Absorption Spectra of the Hydrides and Deuterides of Sulfur, Selenium, and Tellurium and of the Methyl Derivatives of H_2S,* Ibid. **A201**, 600-9 (1950)

(149) W. C. Price, *Recent Advances in Ultraviolet Absorption Spectroscopy,* Repts. Prog. in Phys. **14**, 1-18 (1951)

(150) W. C. Price, *The Absorption Spectra of Molecules in the Vacuum Ultraviolet,* J. Inst. Petroleum **37**, 106-9 (1951)

(151) W. C. Price, J. P. Teegan, and A. D. Walsh, *The Absorption Spectrum of Ketene in the Far Ultraviolet,* J. Chem. Soc. **1951**, 920-6

(152) D. Rakotoarijimy, S. Weniger, and H. Grenat, *Extension of the Schumann-Runge Band System of the Oxygen Molecule into the Near Ultraviolet in Absorption and in Emission,* Compt. rend **246**, 2883-6 (1958)

(153) C. W. Rector, G. W. Schaeffer, and J. R. Platt, *Subsituted Borazole Spectra. Gain and Loss of Aromatic Character,* J. Chem. Phys. **17**, 460-65 (1949)

(154) G. H. Reiling and E. B. Hensley, *Fundamental Optical Absorption in Magnesium Oxide,* Phys. Rev. **112**, 1106-1111 (1958)

(154a) J. Romand and B. Vodar, *Absorption Spectrum of HCl Vapour in the Schumann Region,* Compt. rend. **226**, 238-40 (1948)

(154b) J. Romand and B. Vodar, *Absorption Spectra of HBr and HI in the Schumann Region,* Ibid. **226**, 890-2 (1948)

(155) J. Romand and J. Mayence, *The Absorption Spectrum of Nitrous Oxide in the Schumann Region,* Ibid. **228**, 998-1000 (1949)

(156) J. Romand, *The Absorption of Gaseous HCl, HBr and HI in the Schumann Region,* Ann. phys. **4**, 527-92 (1949)

(157) J. Romand and E. Safory, *Conclusion of the Study of the Ultraviolet Absorption Spectrum of HF Gas,* Compt. rend. **231**, 1050-2 (1950)

(158) J. Romand and B. Vodar, *Absorption Spectra of Benzene in the Vapour State and in Condensed (solid) State in the Far Ultraviolet,* Ibid. **233**, 930-2 (1951)

(159) J. Romand and J. Granier-Mayence, *Effect of Temperature on the Absorption Spectrum of Gaseous Nitrous Oxide Between 2100 and 1600 A,* Ibid. **234**. 824-6 (1952)

(160) J. Romand and J. Granier-Mayence, *Absorption Spectrum of Solid Nitrous Oxide in the Schumann Region,* Ibid. **235**, 1023-5 (1952)

(161) J. Romand and J. Granier-Mayence, *Absorption Spectrum of Solid Oxygen Between 2000 and 1500 A,* J. phys. radium **15**. 62-3 (1954)

(162) J. Romand and B. Vodar, *Contributions to the Study of the Far Ultraviolet,* Spectrochim. Acta **8**, 229-248 (1956)

(163) H. C. Rowlinson and R. F. Barrow, *Absorption Band-Systems of SiO and GeO in the Schumann Region*, J. CHEM. PHYS. **21**, 378-9 (1953)

(164) H. C. Rowlinson and R. F. Barrow, *The Absorption Spectrum of Aluminum Monofluoride in the Schumann Region*, PROC. PHYS. SOC. (LONDON) **A66**, 771-2 (1953)

(165) I. I. Rusoff, J. R. Platt, H. B. Klevens, and G. O. Burr, *Extreme Ultraviolet Absorption of the Fatty Acids*, J. AM. CHEM. SOC. **67**, 673-78 (1945)

(166) E. Safari, *Spectral Study of Hydrofluoric Acid*, ANN. PHYS. **9**, 203-54 (1954)

(167) E. G. Schneider, *A Note on the Photographic Measurement of the Transmission of Fluorite in the Extreme Ultraviolet*, PHYS. REV. **45**, 152-53 1934)

(168) E. G. Schneider, *Optical Properties of Lithium Fluoride in the Extreme Ultraviolet*, IBID. **49**, 341-45 (1936)

(169) E. G. Schneider and H. M. O'Bryan, *The Absorption of Ionic Crystals in the Ultraviolet*, IBID. **51**, 293-98 (1953)

(170) D. Semenow, A. J. Harrison, and E. P. Carr, *Absorption Intensities of the Isomeric Pentenes in the Vacuum Ultraviolet*, J. CHEM. PHYS. **22**, 638-42 (1954)

(171) M. Seya, *Absorption Spectra of Silicon, Oxygen, Nitrogen and Carbon in the Extereme Ultraviolet Region*, SCIENCE OF LIGHT (JAPAN) **1**, 11-18 (1951)

(172) C. H. Shaw and W. T. Foreman, *Ultraviolet Transparent Alkali Metal Filters*, J. OPT. SOC. AM. **49**, 724-28 (1959)

(173) H. Sponer and E. Teller, *Electronic Spectra of Polyatomic Molecules*, REV. MOD. PHYS. **13**, 75-170 (1941)

(174) R. A. Spurr and T. A. Chubb, *Absorption Coefficients of Four Organic Fluorine Compounds in the Vacuum Ultraviolet*, SPECTROCHIM ACTA **10**, 431-2 (1958)

(175) S. Stokes and L. W. Pickett, *Absorption of Bicycloheptane and Bicycloheptene in the Vacuum Ultraviolet*, J. CHEM. PHYS. **23**, 258-60 (1955)

(176) S. Stokes and A. B. F. Duncan, *Electronic Transitions in Methyl Fluorides and in Fluoroform*, J. AM. CHEM. SOC. **80**, 6177-81 (1958)

(177) H. Sun and G. L. Weissler, *Absorption Cross Sections of Carbon Dioxide and Carbon Monoxide in the Vacuum Ultraviolet*, J. CHEM. PHYS. **23**, 1625-8 (1955)

(178) H. Sun and G. L. Weissler, *Absorption Cross Sections of Methane and Ammonia in the Vacuum Ultraviolet*, IBID. **23**, 1160-4 (1955)

(179) H. Sun and G. L. Weissler, *Absorption Coefficients of Nitric Oxide in the Vacuum Ultraviolet*, IBID. **23**, 1372-3 (1955)

(180) L. H. Sutcliffe and A. D. Walsh, *The Vacuum Ultraviolet Spectrum of Allene*, IBID. **19**, 1210 (1951)

(181) L. H. Sutcliffe and A. D. Walsh, *The Ultraviolet Absorption Spectrum of Nitric Oxide*, PROC. PHYS. SOC. (LONDON) **A66**, 209-16 (1953)

(182) T. Takamine, Y. Tanaka, and M. Iwata, *First Ionization Potential of Carbon Monoxide*, SCI. PAPERS, INST. PHYS. CHEM. RESEARCH (TOKYO) **40**, 371-8 (1943)

(183) D. H. Tamboulian and D. E. Bedo, *Metal Foils as Filters in the Soft X-ray Region*, REV. SCI. INSTR. **26**, 747-50 (1955)

(184) Y. Tanaka and T. Takamine, *Vibrational Structure of the Rydberg Series of N_2*, SCI. PAPERS INST. PHYS. CHEM. RESEARCH (TOKYO) **39**, 427-36 (1942)

(185) Y. Tanaka and T. Takamine, *Vibrational Structure* of the *$4\Sigma_g^-(O_2^+) \leftarrow 3\Sigma_g^-$ Rydberg Series of O_2*, IBID. **39**, 437-46 (1942)

(186) Y. Tanaka, *Carbon Monoxide Absorption Spectra in the Extreme Ultraviolet*, IBID. **39**, 447-55 (1942)

(187) Y. Tanaka, *The Extreme Ultraviolet Absorption Spectra of Nitric Oxide*, IBID. **39**, 456-64 (1942)

(188) Y. Tanaka, *Absorption Spectrum of Hydrogen Molecule in the Extreme Ultraviolet*, IBID. **42**, 49-86 (1944)

(189) Y. Tanaka, *On the Absorption Spectrum of Nitric Oxide Molecule in the Extreme Ultraviolet Region II*, J. SCI. RESEARCH INST. (TOKYO) **43**, 160-7 (1949)

(190) Y. Tanaka, M. Seya, and K. Mori, *New Absorption Bands of the NO Molecule in the Extreme Ultraviolet Region*, J. CHEM. PHYS. **19**, 979 (1951)

(191) Y. Tanaka, *On the New Absorption Bands of the Oxygen Molecule in the Far Ultraviolet Region*, IBID. **20**, 1728-33 (1952)

(192) Y. Tanaka, E. C. Y. Inn, and K. Watanabe, *Absorption coefficients of Gases in the Vacuum Ultraviolet IV Ozone*, IBID. **21**, 1651-53 (1953)

(193) Y. Tanaka, *Absorption Spectrum of Nitrogen in the Region from 1075 to 1650 A*, J. OPT. SOC. AM. **45**, 663-64 (1955)

(194) Y. Tanaka, A. S. Jursa, and F. LeBlanc, *Absorption Spectrum of CO in the Vacuum Ultraviolet Region*, J. CHEM. PHYS. **26**, 862-66 (1957)

(195) Y. Tanaka, A. S. Jursa, and F. LeBlanc, *Higher Ionization Potentials of Linear Triatomic Molecules CO_2, CS_2, COS, N_2O*, IBID. **28**, 350-51 (1958)

(196) E. Tannenbaum, E. M. Coffin, and A. J. Harrison, *The Far Ultraviolet Absorption Spectra of Simple Alkyl Amines*, IBID. **21**, 311-18 (1953)

(197) J. P. Teegan and A. D. Walsh, *The Absorption Spectrum of 1:1 Dichloroethylene in the Vacuum Ultraviolet*, TRANS FARADAY SOC. **47**, 1-7 (1951)

(198) K. Teegarden, *Fine Structure in the Exciton Bands of the Alkali Halides*, PHYS. REV. **108**, 660-2 (1957)

(199) D. W. Turner, *Absorption Spectroscopy in the Vacuum Ultraviolet Region*, SCI. J. ROY. COLL. SCI. **26**, 44-61 (1956)

(200) D. W. Turner, *Spectrophotometry in the Far Ultraviolet Region. Absorption Spectra of Some Amides and Cyclic Imides*, J. CHEM. SOC. **1957**, 4555-58

(201) D. W. Turner, *Spectrophotometry in the Far Ultraviolet Region II Absorption Spectra of Steroids and Triterpenoids*, IBID. **1959**, 30-33

(202) M. Ueda, *The Absorption Spectrum of Nitric Oxide in the Far Ultraviolet Region*, SCIENCE OF LIGHT (JAPAN) **3**, 143-55 (1955)

(203) B. Vodar and S. Robin, *Ultraviolet Absorption Spectra of Substances Dissolved in Compressed Gases*, J. CHEM. PHYS. **16**, 996-7 (1948)

(204) B. Vodar and J. Romand, *Recent Progress in the Study of the Far Ultraviolet*, MIKROCHIM. ACTA **1955**, 429-45

(205) P. Wagner and A. B. F. Duncan, *The Absorption Spectrum of Cyclopropane in the Vacuum Ultraviolet Note on the Absorption Spectrum of Methyl Cyclopropane*, J. CHEM. PHYS. **21**, 516-19 (1953)

(206) P. Wagner and A. B. F. Duncan, *The Vacuum Ultraviolet Absorption Spectrum of Difluoromethane*, J. AM. CHEM. SOC. **77**, 2609-10 (1955)
(207) W. C. Walker, O. P. Rustgi, and G. L. Weissler, *Optical Transmission of Evaporated In, Sn, and Bi Films in the Vacuum Ultraviolet*, J. OPT. SOC. AM. **48**, 1017 (1958)
(208) W. C. Walker, O. P. Rustgi, and G. L. Weissler, *Optical and Photoelectric Properties of Thin Metallic Films in the Vacuum Ultraviolet*, IBID. **49**, 471-75 (1959)
(209) A. D. Walsh, *Absorption Spectra of the Chloroethylenes in the Vacuum Ultraviolet*, TRANS FARADAY SOC. **41**, 35-45 (1945)
(210) A. D. Walsh, *Absorption Spectra of Acrolein, Crotonaldehyde and Mesityl Oxide in the Vacuum Ultraviolet*, IBID. **41**, 498-505 (1945)
(211) A. D. Walsh, *Absorption Spectra of 2-Furaldehyde and Benzaldehyde in the Vacuum Ultraviolet*, IBID. **42**, 62-5 (1946)
(212) A. D. Walsh, *Absorption Spectrum of Glyoxal in the Vacuum Ultraviolet*, IBID. **42**, 66-8 (1946)
(213) A. D. Walsh, *The Absorption Spectrum of Acetaldehyde in the Vacuum Ultraviolet*, PROC. ROY. SOC. (LONDON) **A185**, 176-82 (1946)
(214) A. D. Walsh, *The Absorption Spectra of Benzene Derivatives in the Vacuum Ultraviolet II*, IBID. **A191**, 32-8 (1947)
(215) A. D. Walsh, *Far Ultraviolet Spectra and Related Topics*, ANN. REPTS. ON PROGR. CHEM. (CHEM. SOC. LONDON) **44**, 32-49 (1947)
(216) A. D. Walsh, *The Application of Atomic Absorption Spectra to Chemical Analysis*, SPECTROCHIM. ACTA **7**, 108-117 (1955)
(217) K. Watanabe, E. C. Y. Inn, and M. Zelikoff, *Absorption Coefficients of Gases in the Vacuum Ultraviolet*, J. CHEM. PHYS. **20**, 1969-70 (1952)
(218) K. Watanabe and M. Zelikoff, *Absorption Coefficients of Water Vapor in the Vacuum Ultraviolet*, J. OPT. SOC. AM. **43**, 753-55 (1953)
(219) K. Watanabe, E. C. Y. Inn, and M. Zelikoff, *Absorption Coefficients of Oxygen in the Vacuum Ultraviolet*, J. CHEM. PHYS. **21**, 1026-30 (1953)
(220) K. Watanabe, M. Zelikoff, and E. C. Y. Inn, *Absorption Coefficients of Several Atmospheric Gases*, AIR FORCE CAMBRIDGE RESEARCH CENTER TECH. REPT. **53-23**, Cambridge, Mass., June 1953
(221) K. Watanabe and T. Nakayama, *Absorption and Photoionization Coefficients of Furan Vapor*, J. CHEM. PHYS. **29**, 48-51 (1958)
(222) G. L. Weissler, P. Lee, and E. I. Mohr, *Absolute Absorption Coefficients of Nitrogen in the Vacuum Ultraviolet*, J. OPT. SOC. AM. **42**, 84-90 (1952)
(223) G. L. Weissler and Po Lee, *Absorption Coefficients of Oxygen in the Vacuum Ultraviolet*, IBID. **42**, 200-3 (1952)
(224) K. Wieland, M. Wehrli, and E. Miescher, *New Band Spectrum of Sulfur in the Schumann Region*, HELV. PHYS. ACTA **6**, 460 (1933)
(225) P. G. Wilkinson and H. L. Johnston, *The Absorption Spectra of Methane, Carbon Dioxide, Water Vapor and Ethylene in the Vacuum Ultraviolet*, J. CHEM. PHYS. **18**, 190-3 (1950)
(226) P. G. Wilkinson and R. S. Mulliken, *Far Ultraviolet Absorption Spectra of Ethylene and Ethylene d_4*, IBID. **23**, 1895-907 (1955)
(227) P. G. Wilkinson, *New Krypton Light Source for the Vacuum Ultraviolet*, J. OPT. SOC. AM. **45**, 1044-46 (1955)
(228) P. G. Wilkinson, *Absorption Spectra of Benzene and Benzene d_6 in the Vacuum Ultraviolet*, CAN. J. PHYS. **34**, 596-615 (1956)
(229) P. G. Wilkinson, *Absorption Spectra of Ethylene and Ethylene d_4 in the Vacuum Ultraviolet II*, IBID. **34**, 643-52 (1956)
(230) P. G. Wilkinson, *High Resolution Absorption Spectra of Nitrogen in the Vacuum Ultraviolet*, ASTROPHYS. J. **126**, 1-9 (1957)
(231) P. G. Wilkinson, *A High Resolution Spectrograph for the Vacuum Ultraviolet*, J. MOL. SPECTROSCOPY **1**, 288-305 (1957)
(232) P. G. Wilkinson, *Absorption Spectra of Acetylene and Acetylene d_2 in the Vacuum Ultraviolet*, IBID. **2**, 387-404 (1958)
(233) R. W. Wood, *Remarkable Optical Properties of the Alkali Metals*, PHYS. REV. **44**, 353-60 (1933)
(234) R. E. Worley and F. A. Jenkins, *A New Rydberg Series in N_2*, IBID. **54**, 305 (1938)
(235) R. E. Worley, *Absorption Spectrum of N_2 in the Extreme Ultraviolet*, IBID. **64**, 207-224 (1943)
(236) R. E. Worley, *A Third Rydberg Series of N_2*, IBID. **89**, 863-4 (1953)
(237) M. Zelikoff and K. Watanabe, *Absorption Coefficients of Ethylene in the Vacuum Ultraviolet*, J. OPT. SOC. AM. **43**, 756-759 (1953)
(238) M. Zelikoff, K. Watanabe, and E. C. Y. Inn, *Absorption Coefficients of Gases in the Vacuum Ultraviolet. II. Nitrous Oxide*, J. CHEM. PHYS. **21**, 1643-7 (1953)

Supplement

(239) J. Barrett and A. L. Mansell, *Ultraviolet Absorption Spectra of the Molecules H_2O, HDO and D_2O*, NATURE **187**, 138 (1960)
(240) J. M. Bologna, O. K. Larison, D. L. Randall, and D. L. Ringwalt, *An Airborne Lyman α Humidiometer*, N.R.L. REPT. **5180**, Aug. 12, 1958
(241) A. E. Douglas and K. S. Rao, *A New Band System of the P_2 Molecule Analogous to the Lyman-Birge-Hopfield Bands of N_2*, CAN. J. PHYS. **36**, 565-570 (1958)
(242) W. R. S. Garton, *Investigations of Atomic and Molecular Absorption Spectra. III. Ultraviolet Absorption Spectra of Indium Vapor*, PROC. PHYS. SOC. (LONDON) **A67**, 864-868 (1954)
(243) F. A. Gunther, J. H. Barkley, M. J. Kolbezen, R. C. Blinn, and E. A. Staggs, *Quantitative Microdetermination of Gaseous Ammonia by its Absorption at 204.3 mμ*, ANAL. CHEM. **28**, 1985-89 (1956)
(244) G. Herzberg and T. J. Hugo, *Forbidden Transitions in Diatomic Molecules. CO*, CAN. J. PHYS. **33**, 757-772 (1955)
(245) G. Herzberg and J. Shoosmith, *Absorption Spectrum of Free CH_3 and CD_3 Radicals*, IBID. **34**, 523-525 (1956)
(246) G. Herzberg, *Lamb Shift of the 1^2S Ground State of Deuterium*, PROC. ROY. SOC. (LONDON) **234A**, 516-528 (1956)
(247) G. Herzberg and K. K. Innes, *Ultraviolet Absorption Spectra of HCN and DCN. I. The α-x and β-x Systems*, CAN. J. PHYS. **35**, 842-879 (1957)
(248) H. B. Klevens and J. R. Platt, *Survey of Vacuum Ultraviolet Spectra of Organic Compounds in Solution*, TECH. REPT. 1953-54, ONR Contract N60R1-20, Task Order IX, Project NR 019, 101

(249) E. Lyons and G. C. Morris, *The Absorption Spectrum of Anthracene Vapor from 36,000 to 66,000 cm⁻¹*, J. MOL. SPECT. **4**, 480-487 (1960)

(250) W. C. Price, W. F. Sherman, and G. R. Wilkinson, *The Influence of Environment Upon the Spectra of Molecules in Liquids and Crystals*, PROC. ROY. SOC. (LONDON) **A255**, 5-21 (1960)

(251) W. C. Price, P. V. Harris, G. H. Beaven, and E. A. Johnson, *Ultraviolet Absorption Spectra of the Molecules H_2O, HDO, and D_2O*, NATURE **188**, 45-46 (1960)

(252) K. Stich, G. Rotzler, and T. Reichstein, *Characterization of Primary Unsaturated Steroids Through Their Short Wavelength Ultraviolet Absorption Spectra*, HELV. CHIM. ACTA **42**, 1480-1502 (1959)

(253) D. W. Turner, *Far Ultraviolet Light Absorption By Saturated Hydrocarbons*, CHEM. & IND. (LONDON) **1958**, 626-627

(254) P. G. Wilkinson and T. Tanaka, *A New Xenon Light Source For the Vacuum Ultraviolet*, J. OPT. SOC. AM. **45**, 344-349 (1955)

(255) P. G. Wilkinson and R. S. Mulliken, *Dissociation Processes in Oxygen above 1750 A*, ASTROPHYS. J. **125**, 594 (1957)

(256) P. G. Wilkinson, *Forbidden Band Systems in Nitrogen. I. The Vegard-Kaplan System in Absorption*, J. CHEM. PHYS. **30**, 773-776 (1959)

Submitted April 28, 1960

Infrared and Ultraviolet Absorption Spectra of Alpha-Azido Ethers and Amines†

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Abstract

The ultraviolet absorption spectra of a series of alpha- azido ethers, alpha- azido thioethers, and alpha- azido amines exhibited extinction coefficient maxima in the region 264-300 mμ. A shift to the lower wavelength was found to occur in the order S>O>N when these atoms are substituted alpha to an azido- group.

Infrared absorption spectra were recorded in the 2 to 15 micron region, and assignments made for the asymmetric and symmetric N_3 stretching vibrations. The N_3 asymmetric vibration occurred in the range 2141-2090 cm^{-1} for the azides examined. The N_3 symmetric vibration was more variable. Tentative assignments were made for this absorption occurring for alpha- azido ethers and alpha- azido thioethers. However, no assignment was made for this vibration for the alpha-azido amines due to the complicated spectra in this region. The N_3 asymmetric vibration for azidomethyl methyl ether, azidomethyl methyl sulfide and N-azidomethyl phthalimide exhibited a doublet while other azides exhibited a single absorption for this mode.

Introduction

The linear structure of the azido-group, as in covalent and ionic azides, coupled with its facility of forming five membered azoles of structure I:

I

where A is carbon and B may be carbon, nitrogen or sulfur, respectively, has led to questions concerning the nature of the intermediate state. The basic question to be answered involves the process whereby three sequentially linked nitrogen atoms changes from the linear structure to the bent structure. The present investigation is part of a program which attempts to study this problem.

The use of absorption spectroscopy to the solution of structural problems in the thiatriazole ring system has been reported by Lieber and students *(1-4)*. It was demonstrated that reactions which should lead to thiocarbamyl azides are in reality derivatives of the thiatriazole ring system. Infrared spectral evidence confirmed this *(1-7)*. On the other hand, spectroscopic evidence just as clearly demonstrates the existence of the carbamyl azide structure rather than the oxytriazole ring system. Scott *(8)* reported a broad clean asymmetric N_3 absorption band in the infrared for a number of phosphoryl azides and concluded that a ring structure does not exist.

Azides are reported *(9)* to be readily recognized by the strong N_3 asymmetric stretching absorption, which occurs with constancy near 2130 cm^{-1}. The corresponding symmetric stretching occurs at a considerably lower frequency (about 1300 cm^{-1}) but is much more variable in frequency and intensity. Contributions to the infrared absorption spectroscopy of azides have been made by Eyster *(10)*, Sheinker *(11)*, Boyer *(12,13)* Lucien *(14)* and Lieber *(15,16)*. More recently, Lieber *(17)* has discovered that aromatic acid azides exhibit a doublet for the N_3 asymmetric stretching absorption. An extension of this work *(23)* demonstrated that the N_3 *asymmetric doublet* was due to the proximity of the conjugative aromatic unsaturation (benzene ring) and that the band again appeared as a *singlet* when the aromatic ring was reduced, as in *cyclohexyl carboxylic acid azide.* It was with the objective of studying such *alpha interactions* (which the authors now term *perturbation effects)* that the investigation of the absorption spectroscopy of alpha-azido ethers and amines was initiated. These compounds can be generalized by the structure: R-X-CH_2-N_3, where X may be oxygen, sulfur, or nitrogen and R is an alkyl or aryl group, respectively. The similarity of these compounds to thiocarbamyl azides, carbamyl azides, and carbonyl azides may be ob-

†The studies reported in this paper were supported by the Basic Research Group, Military Engineering Department, The Engineer Center, U. S. Army, Fort Belvoir, Virginia. The authors gratefully acknowledge this support.

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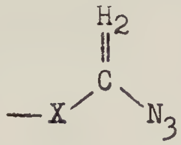
served by rewriting the structure in the following form given by:



where X = O, S, or N, in which the *perturbating effect* is limited to the oxygen, sulfur or nitrogen atoms, respectively. A systematic study of the ultraviolet and infrared absorption spectra of alpha azide ethers has not been previously reported.

Experimental*

Alpha-Azido Ethers and Amines

In general, these compounds were prepared by the action of sodium azide upon the corresponding alpha-haloether as described by Böhme for alpha-azido-ethers *(18)*, alpha-azido thio ethers *(19)* and N-azido-methylamines *(20)*. The compounds prepared for spectroscopic study are summarized in Table I. In most cases satisfactory elemental analyses for carbon and hydrogen were obtained. Unlike that reported by Böhme *(18)* the methyl- and ethyl- alpha-azido ethers proved to be too explosive for carbon and hydrogen combustion. In the case of the alpha-azido thioethers satisfactory elemental sulfur analyses were obtained in all cases. *Bis*-azido-methyl sulfide, a new compound, proved to be too explosive for carbon-hydrogen analysis. All of the compounds reported in Table I are liquids, except that of N-azidomethylphthalimide, a new compound, which comprised colorless plates, melting at 72-73° (uncorrected). All of the liquids had boiling points which agreed with the values previously reported *(18-20)*. *Alpha-azido ethers and amines are dangerous compounds. Repetitions of these synthesis should observe proper safety equipment including spark-proof stirring motors.*

TABLE I. ALPHA-AZIDO ETHERS AND AMINES
$R\text{-}X\text{-}CH_2\text{-}N_3$

R	*X*	*Formula*	*Nitrogen, %* *Calcd.*	*Found*
CH_3	O	$C_2H_5N_3O$[a]	48.26	48.26
C_2H_5	O	$C_3H_7N_3O$[a]	41.56	41.20
CH_3	S	$C_2H_5N_3S$	40.74	40.03
C_2H_5	S	$C_3H_7N_3S$	35.86	35.80
n-C_3H_7	S	$C_4H_9N_3S$[b]	32.03	32.35
C_6H_5	S	$C_7H_7N_3S$	25.43	25.43
$C_6H_5CH_2$	S	$C_8H_9N_3S$	23.44	23.75
N_3CH_2	S	$C_2H_4N_6S$[a,b]	58.30	58.50
$(CH_3)_2$	N[e]	$C_3H_8N_4$	55.97	55.65
C_5H_{10}	N[c]	$C_6H_{12}N_4$	39.97	40.30
$C_6H_4C_2O_2$	N[d]	$C_9H_6O_2N_4$[b]	27.71	27.65

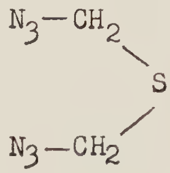
[a]Three independent analytical laboratories were unable to analyze for carbon and hydrogen due to the very explosive thermal degradations of the compounds when heated.
[b]New compounds
[c]Piperidino-group
[d]Ortho-phthalimido-group
[e]Böhme (20) was unable to obtain a satisfactory analysis for this compound.

*Elemental micro-analyses were carried out by Dr. C. Weiler and Dr. F. B. Strauss, Oxford, England.

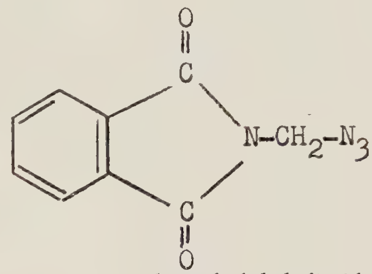
TABLE II. ULTRAVIOLET ABSORPTION FREQUENCIES FOR $R\text{-}X\text{-}CH_2\text{-}N_3$

RX	λ_{max}, $m\mu$	ε_{max}
CH_3O	274	39.9
CH_3CH_2O	276	33.1
CH_3S	284	28.0
CH_3CH_2S	284	28.4
$CH_3CH_2CH_2S$	284	29.8
N_3-CH_2-S	284	54.9
C_6H_5S	[a]	[a]
$C_6H_5CH_2S$	[a]	[a]
$(CH_3)_2N$	264[b]	32.6
$C_5H_{10}N$	264[b]	37.7
$C_6H_4C_2O_2N$	[a]	[a]

[a]Azide absorption in the 260-290 $m\mu$ region masked by strong aromatic absorption.
[b]λ_{max} taken as the inflection point.



Bis-azido-methyl sulfide



N-Azidomethylphthalimide

Ultraviolet Absorption Spectra

Spectra were obtained on a Beckman Model DU quartz spectrophotometer with 1 cm matched quartz cells over the range of 240-300 $m\mu$ and curves plotted for log ε versus wave length. All samples were dissolved in anhydrous spectroscopic methanol, and absorbance readings using a methanol blank were taken. Anhydrous conditions were rigidly maintained. The data obtained are summarized in Table II. Figure 1 shows a typical plot for each of the three different types of azido-ether.

Infrared Absorption Spectra

The spectra were recorded on a Perkin-Elmer Model 21 double beam spectrophotometer with a sodium chloride prism (calibrated against a polystyrene film) over the range of 2-15 microns using an automatic slit drive with a program of 927 and a scanning rate of twenty min. The spectra of liquids were recorded in a demountable cell containing a 0.025 mm silver spacer. Solids were mulled in a drop or two of white oil (Nujol). Spectra over selected ranges were recorded from solution by nulling out the solvent spectra in the reference beam. Exact N_3 asymmetric absorption frequencies were recorded from carbon tetrachloride solution in 0.20 mm matched cells with a program of 960, adjusting the concentration so as to absorb 70-80% of the energy input at the absorption maximum. Because of the complicated vibrations appearing in the N_3 symmetric stretching region, this portion of the spectrum was also recorded in carbon tetrachloride. Spectra of the halomethyl intermediate were also recorded from solution and super imposed on the azido spectra in order to locate the N_3 symmetric stretching absorption. The infrared assignments for the N_3 asymmetric and symmetric vibration are summarzied in Table III. A typical full scale spectrum is shown by Figure 2 for azidomethyl methyl sulfide. The more precise study in the asymmetric region for the same compound is shown in Figure 3, which shows the asymmetric doublet. The complexity of the symmetric region is illustrated by bis-(azido methyl) sulfide in Figure 4.

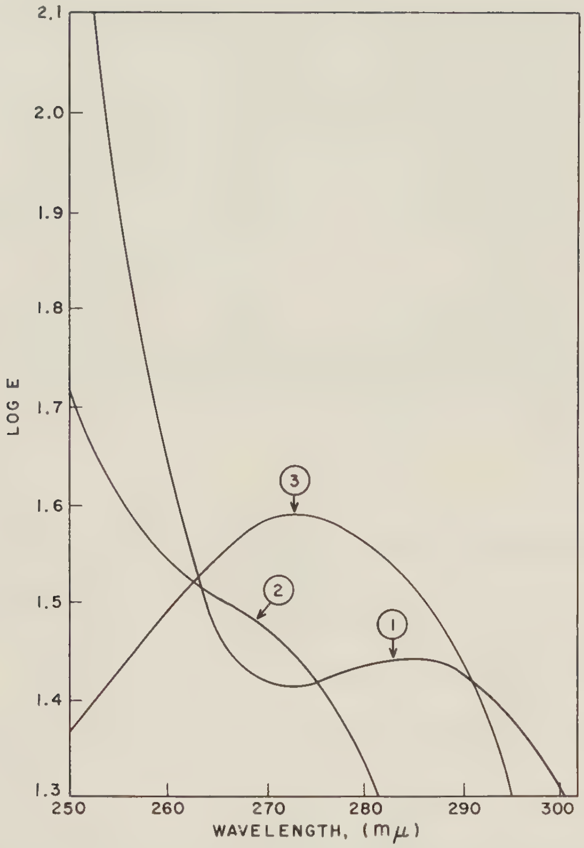


FIG. 1. ULTRAVIOLET ABSORPTION SPECTRA OF (1) Azidomethyl methyl sulfide, (2) N-azidomethyl dimethylamine, and (3) Azidomethyl methyl ether.

Discussion

Ultraviolet Absorption Spectra

Gilliam and Stern *(21)* report that aliphatic azides such as ethyl azide or azidoacetic acid show a characteristic low intensity band near 285 mμ (E = 20-50) and a band of high intensity near 222 mμ (E ca. 150) and that this band differs from that of azide ion, e.g., sodium azide. Lieber *(22)* has reported a weak absorption band between 282 and 288 mμ for a number of alphatic and aromatic azides. The intensity of this band was very weak, and an increase in chain length did not effect the intensity of this band. The absorption was stronger in the phenyl and substituted phenyl azides, although not as strong as the primary band of benzene. Böhme *(18,19)* reported the presence of a weak band for azido-methyl ethers and azidomethyl thioethers in the 275-290 mμ region.

As seen in Table II, spectra of azidomethyl ethers, -thioethers, and -amines exhibited absorptions of weak intensity in the 264-284 mμ region. A shift toward the lower wavelength is seen to occur in the order S>O>N (Figure 1), when these atoms are substituted alpha to an azido group. An increase in chain length had little effect upon the intensity of this absorption. However, the introduction of a second azido group into a molecule increased the intensity of this absorption nearly two fold. Spectra of aromatic azides were not plotted, since the primary aromatic bands overshadowed the weaker azide absorption. As in the past, absortpions in this region are assigned to the nitrogen -nitrogen multiple linkages of covalently bound azides. However, the effect of the substituent alpha to the azido group is seen by a shift of the azide absorption. Although limited in scope, this appears to be the first systematic study of the effect of an alpha substituent on the ultraviolet azido frequency.

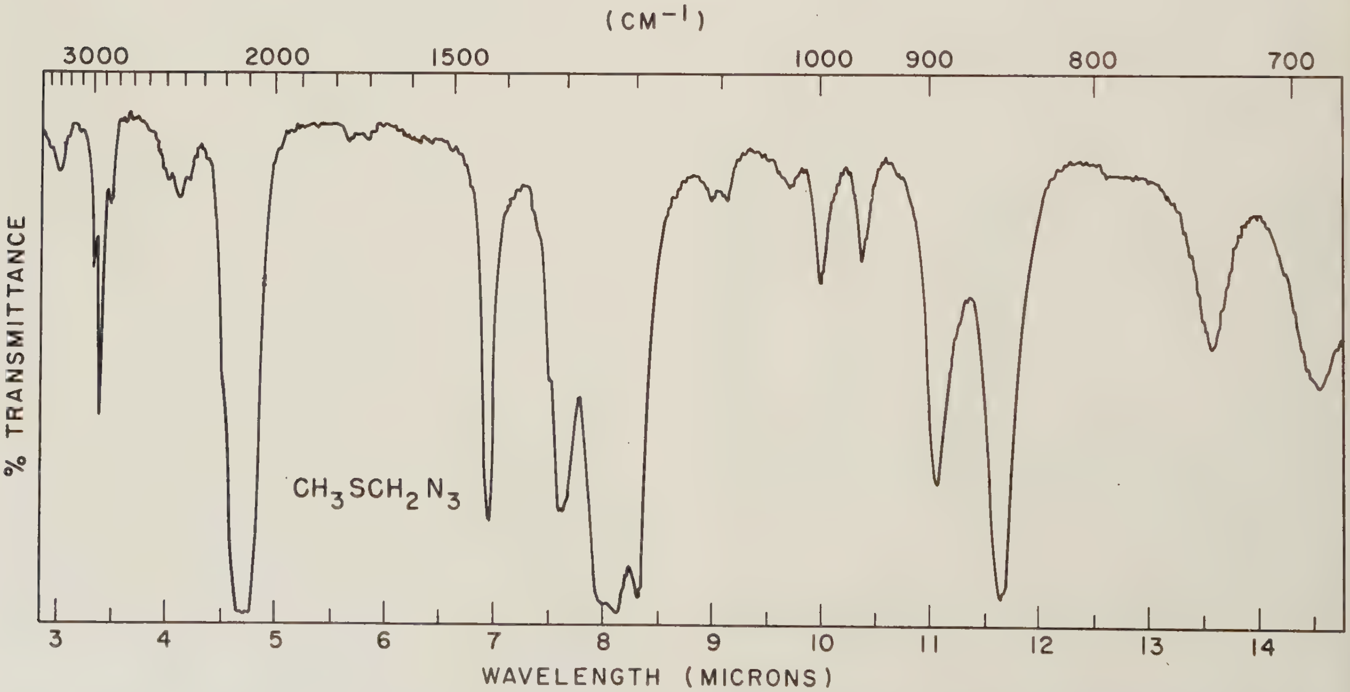


FIG. 2. INFRARED ABSORPTION SPECTRA OF LIQUID AZIDOMETHYL METHYL SULFIDE IN 0.025 MM CELL:

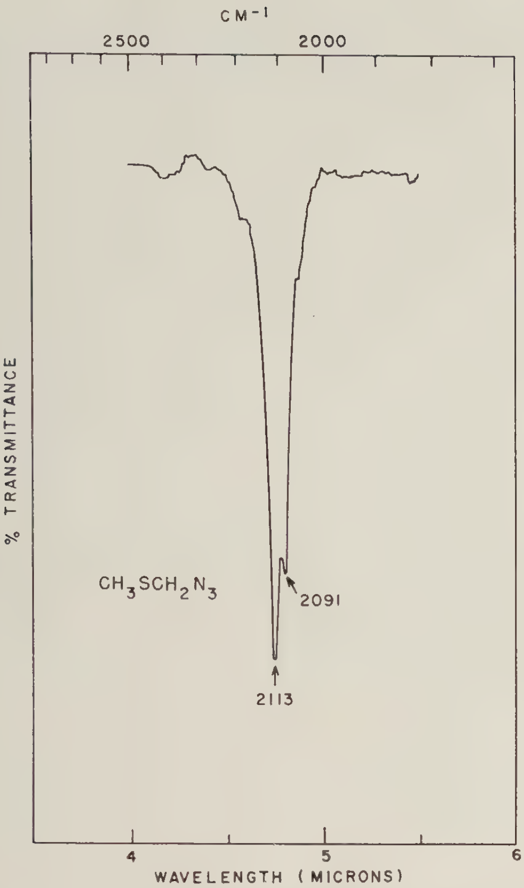


Fig. 3. The Infrared Absorption Spectra of Azidomethyl Methyl Sulfide in the Asymmetric N_3 Region Recorded as a Solution in Carbon Tetrachloride

Infrared Absorption Spectra

The infrared absorption spectra of azidomethyl ethers, -thio-ethers, and -amines were studied with particular emphasis upon the N_3 asymmetric and symmetric vibrations. The spectra of azidomethyl ethers, -thioethers, and -amines were recorded and compared to the spectra of the corresponding halomethyl compounds. A strong broad band exhibiting 100% absorption was observed in the N_3 asymmetric stretching region for all azide spectra with but a single exception. N-azidomethyl phthalimide exhibited a doublet in this region as well as in the carbonyl region. Alpha-halo methyl compounds have no significant absorptions in the N_3 asymmetric stretching region. The N_3 symmetric stretching region was complicated by the presence of other absorptions. However, tentative assignments were made when possible.

The spectra of azidomethyl ethers -thioethers and -amines were recorded in carbon tetrachloride solution across the N_3 asymmetric stretching region (Figure 3). Assignments for the N_3 asymmetric stretching absorption are summarized in Table III. This absorption occurred in the range 2141-2090 cm^{-1} for the azides examined, with all but one falling in the range 2121-2091 cm^{-1}; thus confirming the constancy of the N_3 asymmetric stretching band regardless of environmental groups as reported by previous workers *(15,17)*.

It is interesting to note the band splitting of the N_3 asymmetric stretching absorption for azidomethyl methyl ether and azidomethyl methyl sulfide (Figure 3), when

Fig. 4. Infrared Absorption Spectra in the Symmetric N_3 Region Recorded with Solutions in Carbon Tetrachloride. Solid Line—Bis-(azidomethyl) sulfide, Dotted Line—Bis-(chloromethyl) sulfide

these azides are present in a concentration low enough to keep the absorption on scale. Higher homologues of these azides failed to show this band splitting, but exhibited a single N_3 asymmetric stretching absorption (Table III). The corresponding N-azido-methyl amines exhibited a single absorption, with the exception of N-azido-methyl phthalimide whose doublet was also evident from a Nujol mull as described earlier.

Hydrazoic acid, in the gaseous state exhibited a doublet for the N_3 asymmetric stretching mode *(23)*, a solution of hydrazoic acid in carbon tetrachloride was prepared,

TABLE III. INFRARED ASSIGNMENTS FOR N_3 ASYMMETRIC AND SYMMETRIC STRETCHING VIBRATIONS

Azide	*Asymmetric N_3 Stretching*[a]	*Symmetric N_3 Stretching*[a] *(tentative)*
$CH_3OCH_2N_3$	2121vs, 2098vs	1232s
$CH_3CH_2OCH_2N_3$	2119vs	1227s
$CH_3SCH_2N_3$	2113vs, 2091vs	1304-1294m
$CH_3CH_2SCH_2N_3$	2098vs	1302m
$CH_3CH_2CH_2SCH_2N_3$	2105vs	1299m
$C_6H_5SCH_2N_3$	2101vs	1304-1295m
$C_6H_5CH_2SCH_2N_3$	2107vs	1309-1295m
$N_3CH_2SCH_2N_3$	2112vs	1304-1292s
$(CH_3)_2NCH_2N_3$	2094vs	b
$C_5H_{10}NCH_2N_3$	2094vs	b
$C_6H_5C_2O_2NCH_2N_3$	2140s, 2104s	b

[a]In cm^{-1}; vs, very strong, etc.
[b]Spectrum is complicated by the presence of other absorptions and no assignment can be made.

and the spectrum recorded with a single N_3 asymmetric stretching absorption observed for this spectrum.

The spectra of these azides and the corresponding halo compounds were recorded from carbon tetrachloride solution across the N_3 symmetric stretching region (Figure 4). While this band is complicated by the presence of other absorptions in the region, tentative assignments are made for this mode and appear in Table III.

The spectra of azidomethyl methyl sulfide and azidomethyl ethyl sulfide were recorded as solutions of methanol and acetonitrile as well as carbon tetrachloride with no noticeable changes in the N_3 asymmetric stretching absorptions.

The reason for the absence of band splitting for other members of the series of compounds studied is not clearly understood. A theoretical study of the above systems from a quantum mechanical point of view is underway which will be reported upon in a separate communication.

Literature Cited

(1) E. Lieber, E. Oftedahl, C. N. Pillai, and R. D. Hites, J. ORG. CHEM. **22**, 441 (1957)
(2) E. Lieber and C. N. Pillai, IBID. **22**, 1054 (1957)
(3) E. Lieber, C. N. Pillai, J. Ramachandran, and R. D. Hites, IBID. **22**, 1750 (1957)
(4) E. Lieber, C. N. Pillai, and R. D. Hites, CAN. J. CHEM. **35**, 832 (1957)
(5) P. A. Smith, Private Communication
(6) K. A. Jensen, Private Communication
(7) F. L. Scott, EXPERIENTIA **13**, 275 (1957)
(8) F. L. Scott, Private Communication
(9) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, New York, 1958
(10) E. H. Eyster, J. CHEM. PHYS. **8**, 135, 369 (1940)
(11) Y. M. Sheinker and Y. K. Syrkin, IZVEST. AKAD. NAUK. S.S.S.R. SER. FIZ. **14**, 478 (1950); C.A. **45**, 3246 (1951)
(12) J. H. Boyer, J. AM. CHEM. SOC. **73**, 5248 (1951)
(13) J. H. Boyer, J. ORG. CHEM. **23**, 1051 (1958)
(14) H. W. Lucien, J. AM. CHEM. SOC. **80**, 4458 (1958)
(15) E. Lieber, D. R. Levering, and L. J. Patterson, ANAL. CHEM. **23**, 1594 (1951)
(16) E. Lieber, C. N. R. Rao, T. S. Chao, and C. W. W. Hoffman, IBID. **29**, 916 (1957)
(17) E. Lieber and E. Oftedahl, J. ORG. CHEM. **24**, 1014 (1959)
(18) H. Böhme, D. Morf, and E. Mundlos, IBID. **89**, 2869 (1956)
(19) H. Böhme and D. Morf, IBID. **90**, 446 (1957)
(20) H. Böhme and D. Morf, CHEM. BER. **91**, 660 (1958)
(21) A. E. Gilliam and E. S. Stern, *An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry*, Edward Arnold Ltd., London, 1957
(22) E. Lieber, C. N. R. Rao, T. S. Chao, and W. H. Wahl, J. SCI. IND. RESEARCH (INDIA) **16B**, 95 (1957)
(23) A. Dows and G. C. Pimental, J. CHEM. PHYS. **23**, 1258, 1263 (1955)

Submitted August 22, 1960

Notes

Infrared Spectra of Diethylenetriamine and 2-(2-Aminoethylamino)ethanol

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The formation of a coordination compound between diethylenetriamine (DETA) and cellulose has been reported by Segal and Loeb (*4*), and studies have been planned for elucidating the structure and mode of bonding of the complex. X-ray diffraction studies (*4*) indicate that the DETA-cellulose complex, and the complex formed between ethylenediamine (EDA) and cellulose have very similar crystalline interplanar dimensions. Segal and Loeb concluded that the DETA molecule was bonded to the cellulose chain molecules in a manner similar to that accepted for the EDA molecule, this being possible because of a similarity in amine structures. To further pursue the structure study on the complex, another compound, 2-(2-aminoethylamino)ethanol (AEAE), was selected for its structural relationship to DETA and EDA. Infrared spectroscopy was considered to be the best way of obtaining the data needed for elucidating the manner of bonding. However, the study was hampered by lack of information on the infrared spectra of the above amine compounds. In this note the infrared spectra of the amine compounds are presented, and assignments of the observed bands to structural units in the molecule are made.

The DETA was obtained as a commercial product. It was purified by digestion over stick sodium hydroxide, drying with a sodium-lead alloy, and finally distillation. The cut was taken in the boiling range 205-207° C (b.p. (*1*), 207.1° C). The AEAE was a water-white, high-purity product and was used without further purification. The carbon tetrachloride solutions of the amines

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were prepared in a CO_2-free atmosphere (gloved dry box). The concentrations of the solutions were DETA, 28.36 g/1 (0.275 M) and AEAE, 27.75 g/1 (0.27 M).

Absorption spectra* were obtained using a Perkin-Elmer Model 21** double-beam recording infrared spectrophotometer with a sodium chloride prism.

In the following discussion assignment of bands and interpretation of data were made after extensive consultation of several standard texts *(2)*. The DETA and AEAE are related as shown by the structural formulas:

H_2N-CH_2-CH_2-NH-CH_2-CH_2-NH_2, Diethylenetriamine (DETA)

H_2N-CH_2-CH_2-NH-CH_2-CH_2-OH, 2-(2-Aminoethylamino)ethanol (AEAE).

Both of these compounds can be thought of as being N-substituted derivatives of

H_2N-CH_2-CH_2-NH_2, Ethylenediamine (EDA)

where one hydrogen atom in a primary amine group has been replaced, converting the group to a secondary amine. Segal and Loeb *(4)* consider that bonding in the DETA-cellulose complex occurs through this secondary amine group and one primary amine group. The infrared spectra of DETA and AEAE are shown in Figure 1. For the purposes of discussion the spectrum of EDA is also included.

The spectrum of DETA differs significantly from that of AEAE at certain wavelengths as would be expected because of the -OH group. It is quite similar, however, to that of EDA. In fact, from 3413 to 1360 cm^{-1}, the spectra of DETA and EDA are almost identical. This is not surprising if DETA is considered to consist of two EDA moieties, the EDA moiety being that portion of the molecule having the structure H_2N-CH_2-CH_2-NH-. Assignment of EDA bands has already been made in a previous publication *(3)*. The DETA spectrum differs from that of EDA in that there are new absorption bands at 1269, 1133, and 1065 cm^{-1} (7.88, 8.82, and 9.39 microns), and that the EDA bands of 1096, 1051, and 968 cm^{-1} (9.12, 9.51, and 10.33 microns) have disappeared. These shifts have taken place because of the new bond, N-C, which has replaced one N-H bond of EDA. The strong band at 1133 cm^{-1} (8.82 microns) arises from the C_2-N stretching of this secondary amine group. The primary amine C-N stretchings at 1096, 1051 and 1030 cm^{-1} (9.12, 9.51, and 9.70 microns) in EDA are still apparent at 1065 and 1030 cm^{-1} (9.39 and 9.70 microns) in DETA, but the disappearance of the primary amine C-N stretching at 1096 cm^{-1} (9.12 microns) cannot be accounted for. There are still 2 primary amine groups in DETA and therefore it would seem that these vibrations would be unaffected. The 1305 and 1269 cm^{-1} (7.66 and 7.88 micron) bands in DETA are probably -CH_2- deformations and reflect a splitting of the 1298 cm^{-1} -CH_2- band of EDA caused by addition of an EDA moiety to the EDA molecule.

Passing from DETA to AEAE where an OH group replaces an NH_2 group, one observes marked changes in the spectrum. Not only are the -NH_2 and C-N vibrations affected, but the evidence for hydrogen bonding indicates a considerable change in this phenomenon. In the spectrum of DETA the presence of bonded -NH_2 is shown by the

*All spectra were obtained at a rate of 0.5 micron/min with the Resolution dial set at 927, Gain of 6, Response of 1, and Suppression of 3. Cell thickness, NaCl, was 0.48 mm.

**It is not the policy of the Department to recommend the products of one company over those of any others engaged in the same business.

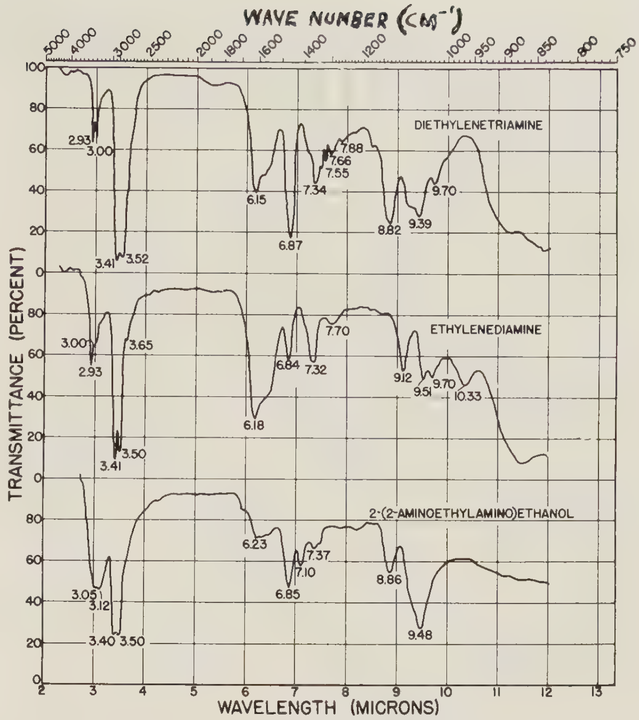

Fig. 1. Infrared Spectra of Diethylenetriamine (DETA), 2-(2-Aminoethylamino)ethanol (AEAE), and Ethylenediamine (EDA)

2 bands at 3413 and 3333 cm^{-1} (2.93 and 3.00 microns), but in the spectrum of AEAE these bands are shifted to 3278 and 3205 cm^{-1} (3.05 and 3.12 microns). Such a large shift to longer wavelengths indicates greatly enhanced bonding which could be expected because of the more electronegative character of the oxygen atom now present. Some contribution to these bands now comes also from bonded -OH stretching vibrations. The more highly associated state produced by the stronger bonding in AEAE is evidenced also by the more viscous nature of the liquid and its higher boiling point, 238-240° C. The C-H stretching bands at 2941 and 2857 cm^{-1} (3.40 and 3.50 microns), the -CH_2- scissoring mode at 1459 cm^{-1} (6.85 microns), and the C-H bending mode at 1356 cm^{-1} (7.37 microns) are the same as in DETA, as would be expected.

The -NH_2 scissoring mode appears at 1605 cm^{-1} (6.23 microns) as a result of the enhanced bonding of the primary amine group and is reduced in intensity as there is now only one such group present. The only absorption band in the spectrum of AEAE attributable solely to the OH group is the -OH bending vibration at 1408 cm^{-1} (7.10 microns). The C-OH stretching of the primary alcohol group is observed in the strong band at 1054 cm^{-1} (9.48 microns), which also includes a primary C-N stretching. The bands near 1130 cm^{-1} and 1060 cm^{-1} (AEAE and DETA) are C-N stretchings of the secondary and primary amine groups, respectively.

The authors are indebted to Mr. R. T. O'Connor for advice and suggestions and to Miss Z. M. Zarins for obtaining the spectra.

Literature Cited

(1) Handbook of Chemistry and Physics, Chemical Rubber, Cleveland, 37th ed., 1956-57

(2) R. N. Jones and C. Sandorfy in *Chemical Applications of Spectroscopy*, W. West, Ed., Interscience

Publishers, New York, 1958, Chap. 2; L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley & Sons, New York, 2nd ed., 1958
(3) L. Segal and F. V. Eggerton, Unpublished Results
(4) L. Segal and L. Loeb, J. POLYMER SCI. **42,** 351 (1960)

Submitted August 8, 1960

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Stable Plasma Jet for Excitation of Solutions†

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The plasma jet, as adapted for the spectrochemical excitation of solutions and used with a photoelectric spectrometer to measure light intensities, provided coefficients of variation of one to two percent *(1)*. A significant portion of the error was attributed to discharge instability. The swirling flow of gas surrounding the jet "flame" at the cathode forces the arc to make electrical contact to the cathode by an arc streamer. It is this streamer moving randomly over the cathode surface which makes the discharge unstable. It appeared that stabilization of the electrical path to give excitation position stability would be necessary to improve the precision of the plasma jet as an excitation source *(2)*.

Various cathode configurations were investigated at Goodyear Atomic Corporation before the use of an external electrode was suggested *(3)*. A consumable graphite electrode (Figure 1) was mounted in a motor-driven device and fed into the jet about 5 mm above the cathode surface. Discharge stability resulted from the elimination of the arc streamer. A decrease in the sound intensity and the arc voltage drop was also achieved. The use of an external electrode for complete or partial electrical return has since been noted for high power plasma jets *(4)*. This mode of operation is generally referred to as "transferred arc". An improved version of the external electrode uses a tungsten rod which is only slowly consumed.

The plasma jet for solution excitation (Figures 2 and 3) has a tungsten rod as an external, yet integral, cathodic electrode. The tungsten rod is electrically connected to the exit orifice electrode and is at ground potential for use with a negatively grounded dc arc power supply. The discharge is initially between the anodic electrode, through which the sample is sprayed into the discharge zone, and the "flame" exit cathodic electrode. As the "flame" contacts the tungsten rod the electrical path transfers to it. After this transfer, the exit orifice electrode is not involved in the arc discharge and consequently does not erode. The tungsten electrode is so slowly consumed that manual adjustment between samples, or every several min, is sufficient. The position of this electrode is not critical as long as the "flame" impinges upon it. If the tungsten does burn away from the "flame", an arc streamer forms back to the exit electrode, and the voltage drop across the device increases.

The jet parts (Figure 4 and Table I) are fabricated of concentric brass and plastic pieces requiring only lathe and brazing operations. While atomizing assemblies can be made from brass stock and stainless steel capillaries, it is simpler to salvage parts from a commercial atomizer-burner*, or the essential parts can be purchased. For use

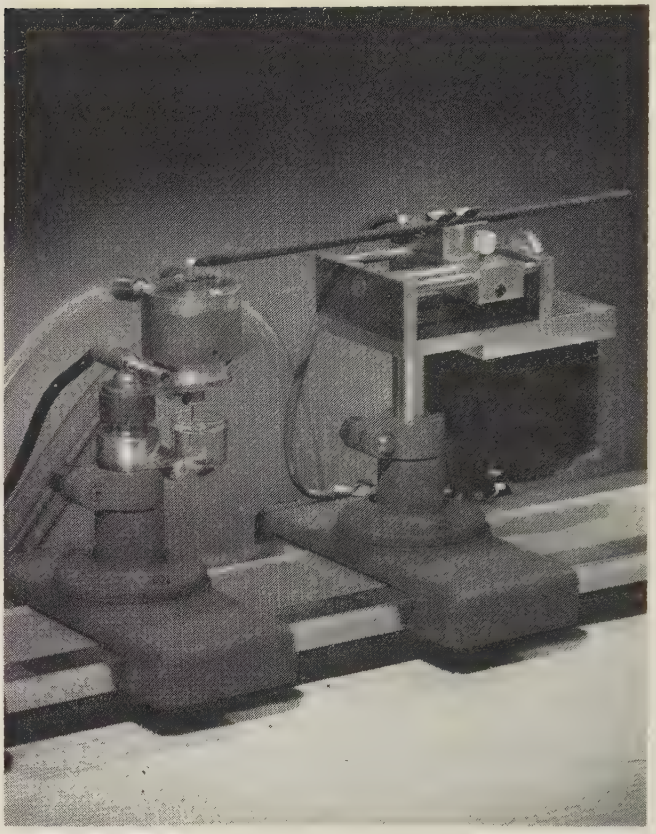

FIG. 1. SOLUTION PLASMA JET WITH GRAPHITE EXTERNAL ELECTRODE

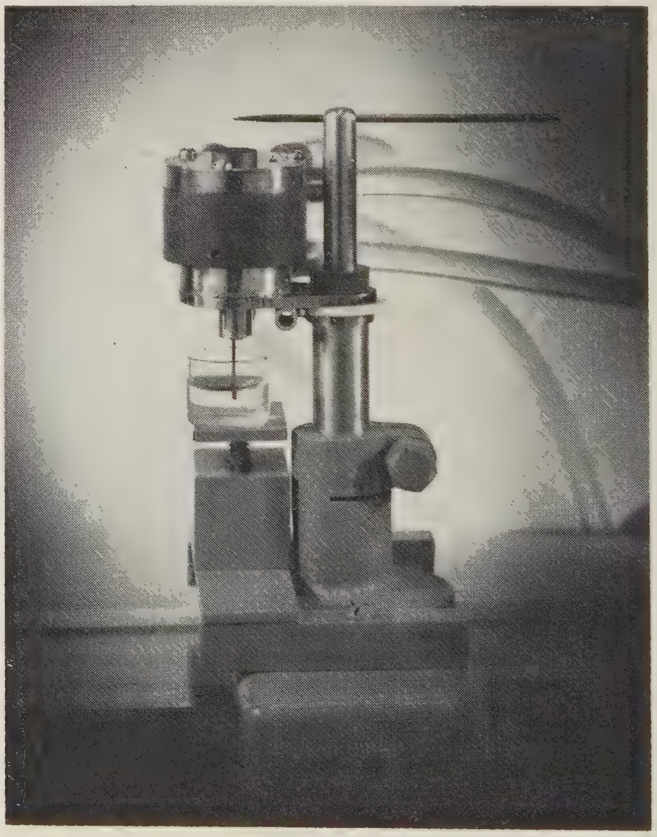

FIG. 2. SOLUTION PLASMA JET WITH TUNGSTEN EXTERNAL ELECTRODE

†This work was performed under Contract AT-(33-2)-1 with the U. S. Atomic Energy Commission.

*Catalog No. 4030, Beckman Instruments, Inc., Fullerton, California

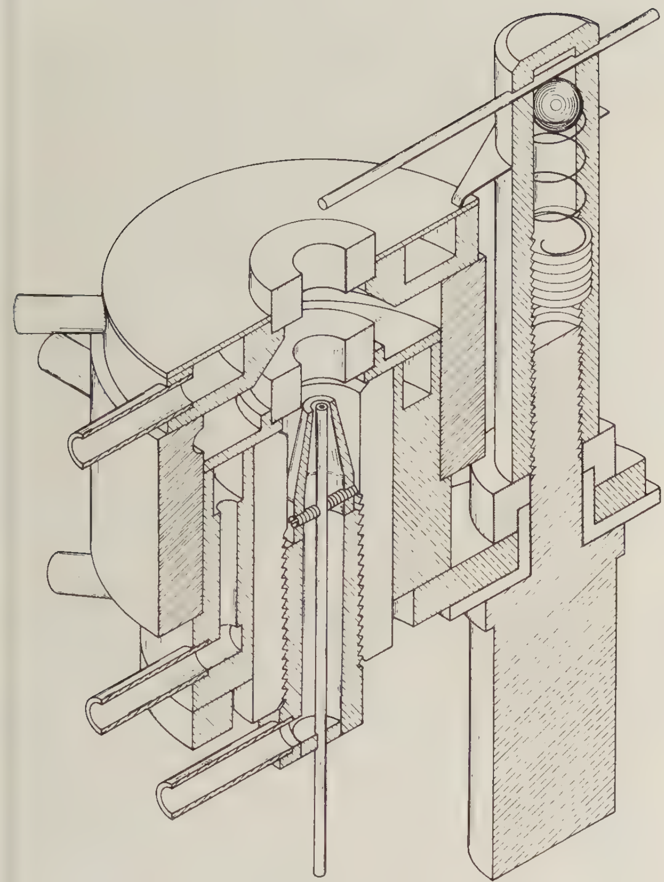

Fig. 3. Sectioned Assembled Solution Plasma Jet

with ungrounded power sources, the support rod of the jet can be plastic with electrical connection made to the post carrying the tungsten electrode.

The general operation of plasma jets has been explained by Margoshes and Scribner *(1)*. For the assembly detailed here, the gas flows are monitored by flowmeters. Twenty l/min of helium are introduced tangentally into the chamber while approximately 3 l/min of argon are used as an atomizer "lift" gas. The argon flow is varied for a particular solution type to provide the sample rate desired. The chamber pressure during operation is around 60 mm of water, but this pressure is not monitored for operational information. A voltage drop of about 95 v occurs with a current of 15 to 25 amps.

Programming controls are used to provide safe and reproducible operation. The argon is supplied in two stages. The initial low flow rate of argon while inadequate for atomization is sufficient to prevent "blow back" of hot gases through the capillary. The programmed operation is: *Step 1*—Tangental helium, low-flow argon, main power and ignition spark are all started. *Step 2*—After a timed delay, or as desired, full argon flow for atomization of the sample is begun. *Step 3*—When the desired excitation period is over, the argon flow is reduced and *Step 4*—After the atomization has ceased, gas and power are removed.

The gas manifold is shown schematically (Figure 5). Solenoid valves *1* and *2* are energized at the beginning of an excitation. Helium flows through a needle valve and flowmeter to the tangental inlet D_1 of the jet. The argon flows through a needle valve and flowmeter to solenoid valve *3*, which initially vents to the atmosphere. Argon also flows through a needle valve to H_1 to protect the

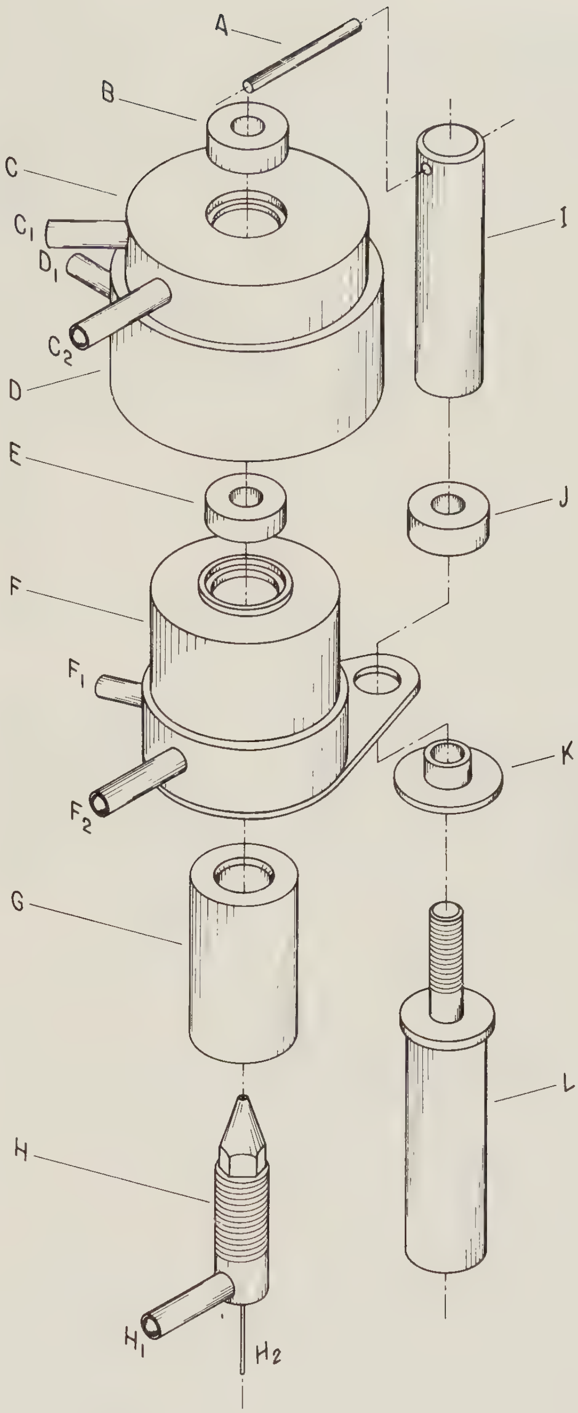

Fig. 4. Exploded View of Solution Plasma Jet

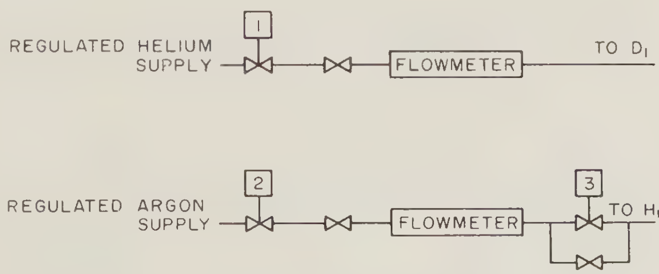

Fig. 5. Gas System for Solution Plasma Jet

TABLE I. COMPONENT PARTS OF SOLUTION PLASMA JET

Key[a]	*Description*	*Material*	*Dimensions*
A	External electrode	Tungsten	3/32 in. o.d. rod
B	Cathode electrode, "Flame" exit point	Graphite	12.5 mm o.d., 5 mm i.d., 5 mm thick
C	Cathode assembly	Brass	1¾ in. o.d., ¼ in. thick
C_1, C_2	Water cooling inlet and outlet	Copper	3/16 in. o.d.
D	Chamber body	Bakelite	1¾ in. o.d., 1-5/32 in. i.d., ¾ in. high
D_1	Tangental gas inlet	Copper	3/16 in. o.d.
E	Anode electrode	Graphite	12.5 mm o.d., 5 mm i.d., 5 mm thick
F	Anode assembly	Brass	Outside diam. to fit inside diam. of chamber body, step edge to give desired separation of graphite electrodes, ⅝ in. i.d.
F_1, F_2	Water cooling inlet and outlet	Copper	3/16 in. o.d.
G	Atomizer assembly insulator	Teflon	⅝ in. o.d., ⅜ in. -24 internal thread
H	Atomizer assembly	Brass	Inner part of Beckman 4030 Atomizer
H_1	Lift gas inlet	Copper	3/16 in. o.d.
H_2	Sample capillary	Platinum sheathed in steel	
I	External electrode holder	Brass	⅜ in. o.d. rod, inside threaded ¼ in. -20
J	Insulating washer	Bakelite	⅝ in. o.d., ¼ in. thick
K	Insulating washer	Teflon	1 in. o.d., ¼ in. thick
L	Support rod	Brass	⅝ in. o.d. (for Bausch & Lomb holders)

[a] Key for Figure 4

atomizer capillary from the arc. When the sample is to be sprayed into the jet, solenoid valve *3* operates to provide the necessary additional argon flow.

It is difficult to make general statements about electrode life, but the graphite electrodes exhibit little electrical erosion and do not contribute to the spectrum even when grossly contaminated. Their longevity is determined by the requirements of a specific analytical procedure. The life of the tungsten electrode is a function of current and time. Several in./hr. may be used at 25 amp. The tungsten electrode does not contribute spectra to the discharge region between it and the graphite electrode.

The stabilized plasma jet promises full utilization of the jet's special inherent feature of high temperature excitation of homogeneous samples which can be reproducibly introduced into its excitation zone. This assumption was borne out when the stabilized version was tested at the National Bureau of Standards with the same spectrometer and comparable solutions as in the original work. With the stabilized jet the limiting factor seems to be the constancy of atomization. With reliable atomization, coefficients of variation of 0.5% or less should be achieved with good reliability.

Literature Cited

(1) M. Margoshes and B. F. Scribner, SPECTROCHIM. ACTA **14,** 138 (1959)

(2) M. Margoshes, *Some Properties of New or Modified Excitation Sources,* in *Symposium on Spectrochemical Excitation.* Special Technical Publication No. **259,** Am. Soc. Testing Materials, Philadelphia, Pa.

(3) R. B. Stambaugh, Personal communication

(4) A. B. Osborn, J. SCI. INSTR. **36,** 317 (1959)

Submitted August 26, 1960

Use of A Getter-Ion Type Pump with A Mass Spectrometer*

A. A. Ebert, Jr.

Jackson Laboratory, Organic Chemicals Department, E. I. du Pont de Nemours & Company, Wilmington, Delaware

A General Electric analytical mass spectrometer has been in use in this laboratory for the past eight years. During this period, most of the down-time experienced with the spectrometer has resulted from failure of the mercury diffusion pump. Such mishaps as burst water lines, broken glass boilers, and broken pump belts have caused the pump to fail often resulting in other damage to the spectrometer. The accumulative effect of pump failures together with associated mishaps have accounted for about 75% of the total down-time.

In addition to the problem of pump failure, a diffusion pump presents a serious maintenance problem. It requires a liquid nitrogen cold trap which must be filled either manually or automatically on a continual round-the-clock basis. Manual filling demands personnel on a daily 24 hr basis. Automatic filling is wasteful of liquid nitrogen and often involves an awkward physical set-up. In either case, the cost of the liquid nitrogen consumed in a year's time becomes significant. In view of these difficulties it seemed desirable to investigate another type pump.

The Varian Vac Ion pump *(1,2)* was investigated because of its many advantages with respect to maintenance. It eliminated the need for a cold trap, cooling water, and a mechanical forepump. The electronic pump had no moving parts, no hot filaments, and no periodically-replaceable components. This obviated the periodic shutdowns required by the diffusion pump for replacing mercury and changing pump oil. The lack of wearable parts assured long life and continuous, uninterrupted service which is essential for optimum mass spectrometer operation.

The life of the pump is a function of the pressure in the system and ultimately depends on the supply of titanium in the pump because titanium is necessary to maintain the pumping action. The economical use of titanium, which has been reported is of interest *(1)*. It has been estimated that in pumping such gases as air, CO_2, and H_2 approximately one half to one gas molecule is pumped for each atom of titanium sputtered. Because of the nature of the pumping mechanism, only as much material is sputtered as is necessary to pump the gas present. With this self-regulating behavior, the pump can be expected to have a life of several years, if it is operated by at very low pressure.

The electronic pump has been in service with the mass spectrometer since October, 1958 and has proved to be completely satisfactory. It produced no difficulty with start-up and reached a good operating range with an overnight pump-down. A pump with a 5 l/sec capacity has been used which pumps a spectrometer volume of about

(Continued on page 154)

*Research Division Contribution No. 301

Spectroscopic Tricks

A Sealed Infrared Absorption Cell of Variable Path Length

E. M. Banas and R. R. Hopkins

Research and Development Department, American Oil Company, Whiting, Indiana

A new infrared absorption cell of variable path length has been devised. As shown in Figure 1, it is similar in construction to cells of fixed path length but has a sample volume in the shape of a circular wedge. The inner surface of one of the windows has impressed into it a circular inclined plane. The outer edge of this surface is flat so that it can be sealed to the flat surface of the other window. The infrared beam passes through the cell midway between its axis and the outside edge. Thus, the effective sample thickness varies as the cell is rotated about its axis. The rotation is measured by a graduated circular scale. No attempt is made to obtain a quantitative sample thickness because the window surfaces enclosing the sample are not parallel.

The depressed surface was obtained by a new technique: plastic deformation of a flat single crystal of an alkali halide. Crystal surfaces were first ground and polished. The crystal was then placed on a flat hot plate, and the temperature was raised at a rate 110°C/hr to 400°C. A metal die, heated to the same temperature as the crystal, was pressed into the crystal surface until the desired depression was obtained. Pressure was released, and the temperature was lowered 110°C/hr.

The cell has several advantages over equipment now in use. The absence of moving parts eliminates gasket seals and the resultant capillary spaces that make cleaning difficult. Spectra can be recorded, on a single filling, over a range of path lengths selected to emphasize details of band structure. Figure 2 shows a portion of the spectrum of tetrahydronaphthalene at the two extremes of path length.

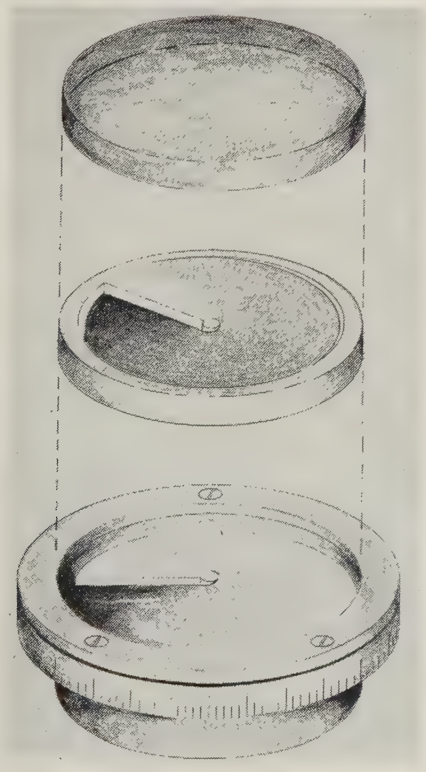

Fig. 1. Cell Assembly

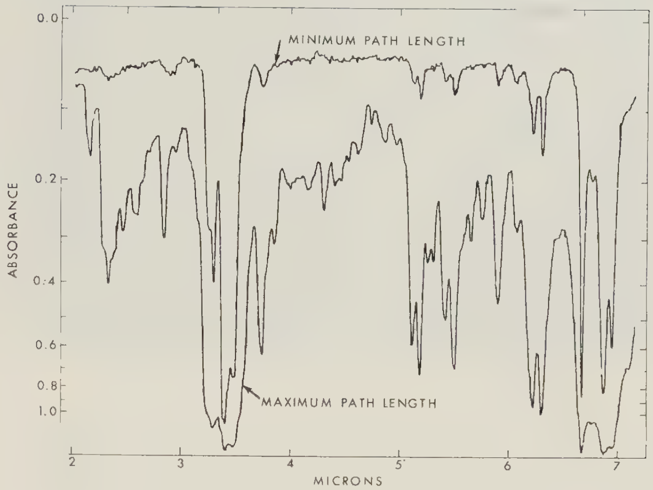

Fig. 2. Infrared Spectrum of Tetrahydronaphthalene

An alternative cell design could be obtained by depressing the crystal surface into steps of different thickness. Such a cell would have a series of different but fixed path lengths and could be used for quantitative analysis. The novel technique of impressing crystals can be applied whenever a surface is desired that can not be obtained easily by grinding and polishing.

Submitted November 16, 1960.

Photo Processing Tank for Spectrographic Plate Development

M. L. Gonshor and S. E. Hausknecht

Kennecott Research Center, Kennecott Copper Corporation, Salt Lake City, Utah

In response to the need for a photo processing unit that would economically fulfill the need for uniform plate or film development, a device was built employing advantages of simplicity, versatility, and ruggedness. Figure 1 shows the unit itself, and the developing tray, plate, and solution beakers are shown in place in Figure 2.

The processor is essentially a stainless steel tank, 18″ x 13″ x 8″ with a 1 in. outlet pipe. This tank can be mounted adjacent to the ordinary darkroom sink or drain. A stainless steel wire tray, 10½″ x 11¼″ x 1″ is attached to the tank with adjustable holding rods to permit depth placement in the water bath as desired. Oscillation of the tray to keep the developing and fixing solution in motion is carried out by means of a synchronous motor† geared down to 5.5 rpm. The oscillation axis is off-center to eliminate the formation of standing waves which could cause Eberhard effect. The motion of the tray serves to give some mixing of the constant-temperature bath water without undue violence. The oscillation stroke is readily adjusted by changing the effective arm length on the motor drive.

†Reversible motor No. PYAZ928-A-1, Barber Coleman Company, Rockford, Ill.

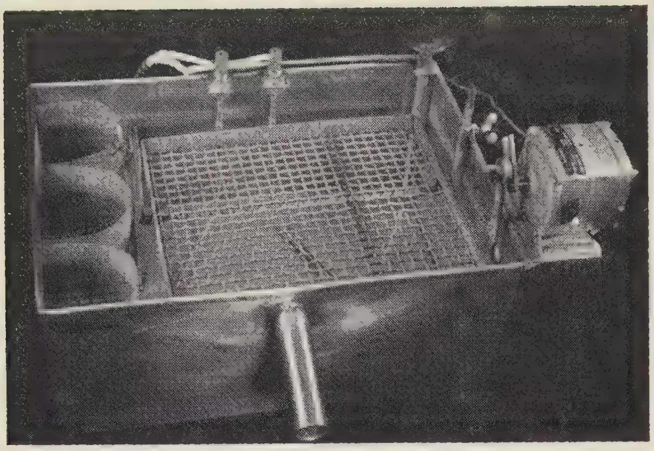

FIG. 1. PLATE DEVELOPMENT TANK

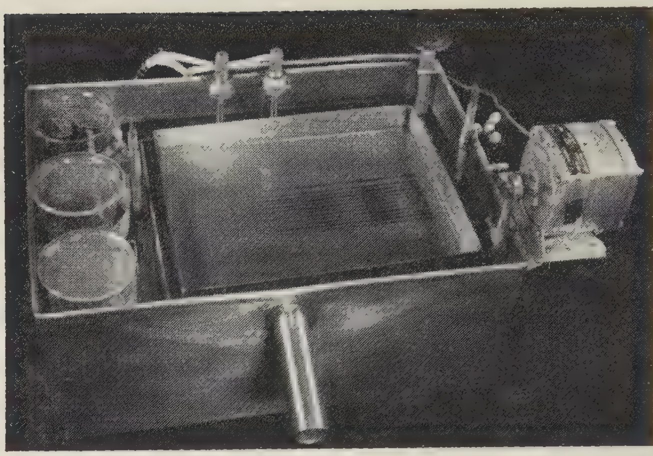

FIG. 2. TANK WITH TRAY, PLATE, AND SOLUTION BEAKERS

Provision is made for controlling the temperature within developing limits. This is accomplished by passing a slow stream of cold water through the bath, and using a bimetallic switch,* to activate a 750 watt enclosed heating unit as needed. The tank is large enough to contain a section where portions of each development solution may be maintained at the proper temperature. A wire screen divides this section from the developer proper to prevent tipping and spilling of solutions.

*Thermoswitch Cat. No. 17502-0, Fenwal Inc., Ashland, Mass.

A single plate tray, 11½" x 4¾" x 1¾", and a double plate tray, 11½" x 9½" x 1¾", also of stainless steel, are used for the plate development. These trays permit the use of a minimum volume (about 150 ml for single plate and 300 ml for double plate) of developer, stop, and fixer. In our laboratory, these used solutions are discarded or used for cases where first quality development is not required.

The depth of the tank is great enough and the adjustment of the tray height is sufficient to permit the accommodation of film development, if desired.

Submitted December 5, 1960

(Continued from page 152)

1.5 l. Between samples, a vacuum of about 1 x 10^{-7} mm Hg is produced. The pump-out time for samples is largely controlled by the speed of evacuation of the expansion chamber, which is pumped by an oil diffusion pump. It normally requires six to seven min to evacuate the expansion chamber, and at the end of this period the analyzer tube is completely clean and ready for the next sample. It would not be feasible to use the electronic pump to evacuate the expansion chamber because of the high pressure involved.

If no samples are introduced into the system for a few hr, or after an overnight pump-out, a vacuum in the 10^{-9} mm range is produced. Pressure in this region cannot be measured precisely because the meter reading is very low or often the needle does not leave its zero position. A reading of 0.1 μa, about the lowest reading possible, corresponds to a pressure of 5 x 10^{-9} mm. These higher vacuum conditions are of significance only with regard to prolonging the life of the pump. If the pump operates in the 10^{-9} mm region the greater part of the day, the pump should last indefinitely.

From an operational standpoint, the principal advantage of the electronic pump is the cleaner spectral background it provides. Mercury is, of course, eliminated, and except for nitrogen and water peaks which are negligibly small no other peaks appear in the background.

Aside from improved backgrounds, little change is noted in general spectrometer performance. Cracking patterns exhibit no anomalies and sensitivities are essentially unchanged. Our experience has shown that sensitivities are largely determined by the conditioning of the ion source, other factors being equal (alignment, focusing, etc.).

The mass spectrometer is used for assistance to general exploratory organic research, and all types of materials have been put through the instrument. Out of a wide range of chemicals examined, none has been encountered that could not be pumped readily, with the exception of inert gases. The pump has worked successfully with hydrocarbons, inorganic gases, halogenated hydrocarbons, strong acids, water vapor, oxygenated compounds, and other organic compounds. Inert gases such as argon and helium are noticeably slower pumping than other materials, and if handled in large quantities over a period of time, they would build up a background. However, if encountered only occasionally in non-excessive amounts ($<50\%$), they produce no problem. It is not recommended that pure argon or helium be admitted to the spectrometer in the usual amounts because they would overload a pump of this size. If these gases are to be analyzed often, a larger pump or several small pumps connected in parallel using the same power supply should be employed. The pump if overloaded by inert gases will overheat and cease to pump and should be shut off when this condition occurs. After about five min cooling, the discharge can be started again, and the pump will quickly produce a good vacuum.

Most of the materials encountered have sufficiently similar pumping rates so that good analytical results can be obtained using conventional sensitivity values. Even materials differing in pumping rates do not seriously affect the accuracy of an analysis as shown in Table I. Although hydrogen has a rated pumping speed about twice that of nitrogen *(3)*, there is no measurable analytical difference in relative concentrations between a blend of butane in hydrogen and butane in nitrogen. This represents an extreme case of differential pumping rates, but no analytical problem is encountered. The results in Table I were computed using sensitivities calculated from a scan of the pure materials. If materials are found differing too widely in pumping rates, they can, of course, be calibrated for the matrix in which they occur.

Table I
Analytical Results on Blends Having Different Pumping Speeds

Blend	Component	Blend, %	Mass Spectrometer Analysis, %
1	Butane	10	9.9
	Nitrogen	90	90.1
2	Butane	10	9.9
	Hydrogen	90	90.1

From the experience gained from its use, the getter-ion type pump appears to be satisfactory for mass spectrometer application and offers many advantages from a maintenance standpoint.

Literature Cited

(1) L. D. Hall, Rev. Sci. Instr. **29**, 367 (1958)
(2) L. D. Hall, Science **128**, 279 (1958)
(3) *VacIon High Vacuum Pump*, Data Sheet V-11402, Varian Associates, Palo Alto, Calif.

Submitted October 18, 1960

Society News

International Conference on Spectroscopy

College Park, Md. June 18-22, 1962

The program committee for the Conference reports that arrangements for the scientific program are advancing on schedule. The address at the opening session on Monday morning, June 18, 1962, will be given by Dr. Jesse Greenstein, California Institute of Technology, who will speak on Astrophysical Spectroscopy.

Authors intending to submit papers for the program are reminded of the topics listed in the earlier release (Applied Spectroscopy **15**, No. 3, 86 (1961)). A time period of 20 minutes for presentation and 5 minutes for discussion will be allotted for each submitted paper that is accepted for the program. Projection of slides in various sizes will be provided and 16-mm film can be projected if requested in advance. Papers may be presented in English, French, or German. However, in view of the fact that practically all of the audience will understand English, it is recommended that papers be given in the English language. Those desiring to present papers should submit titles and abstracts of 250-300 words to the General Chairman before December 31, 1961.

International Advisory Board

This board is composed of spectroscopists who have kindly consented to advise the Conference in planning the program and acting as a contact for their country. The list, to which some additional names may be added, include the following: Dr. N. W. H. Addink, Eindhoven; Dr. W. R. Brode, Washington; Dr. G. Duychaerts, Liege; Prof. Grinfeld, LaPlata; Dr. H. H. Günthard, Zurich; Dr. R. N. Jones, Ottawa; Dr. H. Kaiser, Dortmund; Mr. E. Loeuille, Paris; Dr. A. Mangani, Bologna; Prof. R. Mecke, Freiburg; Dr. W. F. Meggers, Washington; Dr. A. C. Menzies, London; Prof. S. Mizushima, Tokyo; Prof. T. Somiya, Tokyo; Dr. H. Stammreich, Sao Paulo; Dr. H. W. Thompson, Oxford; Dr. B. Vodar, Bellevue; Dr. A. Walsh, Melbourne.

Further details as to the scientific and social program may be obtained upon request to Mr. Bourbon F. Scribner, General Chairman, International Conference on Spectroscopy, National Bureau of Standards, Washington 25, D. C.

Infrared Quantitative Analytical Data

Determination of Acetophenone in Mixtures of Hexene-I and n-Hexane

H. E. MOSELEY, Monsanto Chemical Company, Lion Oil Co. Div., El Dorado, Arkansas

CS-160

Component No.	Name	Formula	Range %	Accuracy %	λ or ν B.L. Pts.	Slit (mm) Δλ or Δν	Conc. % Length (mm)
1	Acetophenone	C_8H_8O	0-60	±1.0	5.93μ	0.045 0.020	5 .041
2	Hexene-1	C_6H_{12}	0-50	±1.0	11.06μ	0.145 0.030	100 .041
3	n-Hexane	C_6H_{14}	0-50	±1.0	13.84μ	0.280 0.052	"

Instrument: Perkin-Elmer Model 21, NaCl Prism
Sample Phase: Liquid
Cell Windows: NaCl
Absorbance Measurement: Base line........... Point......X......
Calculation: Inverted Matrix........... Successive Approx.......X...... Graphical...........

Relative Absorbances—Analytical Matrix:

Component/λ	5.93μ	11.06μ	13.84μ
1	15.760	0.091	0.172
2	0.020	4.150	0.100
3	0.006	0.071	0.330

Material Purity: Acetophenone - Eastman 99%+; Hexene-1 and n-Hexane - Phillips Pure Grade 99 mole % minimum

Comments: Dilutions, when necessary, in Carbon Disulfide. Relative absorbances are given as the slope of the Beer's Law concentration curves used and are expressed in terms of absorbance per 100% of constituent.

Determination of Acetophenone in Mixtures of Decene-I and n-Decane

H. E. MOSELEY, Monsanto Chemical Company, Lion Oil Co. Div., El Dorado, Arkansas

CS-161

Component No.	Name	Formula	Range %	Accuracy %	λ or ν B.L. Pts.	Slit (mm) Δλ or Δν	Conc. % Length (mm)
1	Acetophenone	C_8H_8O	0-60	±1.0	5.93μ	0.045 0.020	5 .041
2	Decene-1	$C_{10}H_{20}$	0-50	±1.0	11.03μ	0.145 0.030	100 .041
3	n-decane	$C_{10}H_{22}$	0-50	±1.0	13.90μ	0.294 0.055	"

Instrument: Perkin-Elmer Model 21, NaCl Prism
Sample Phase: Liquid
Cell Windows: NaCl
Absorbance Measurement: Base line........... Point......X......
Calculation: Inverted Matrix........... Successive Approx......X...... Graphical...........

Relative Absorbances—Analytical Matrix:

Component/λ	5.93μ	11.03μ	13.90μ
1	15.760	0.091	0.140
2	0.028	3.150	0.350
3	0.020	0.051	0.408

Material Purity: Acetophenone - Eastman 99%+; Decene-1 and n-Decane - Humphrey-Wilkinson 98%+

Comments: Dilutions, when necessary, in Carbon Disulfide. Relative absorbances are given as the slope of the Beer's Law concentration curves used and are expressed in terms of absorbance per 100% of constituent.

S.A.S. Local Section News

Editor—Carl J. Leistner

[Items for this column should be sent to the Editor, Mr. Carl J. Leistner, United Carbon Products Company, P. O. Box 747, Bay City, Michigan.]

1961 Eastern Analytical Symposium and Instrument Exhibit

Statler Hilton Hotel

New York City November 15, 16, and 17, 1961

The 1961 Eastern Analytical Symposium will be held at the Statler Hilton Hotel in New York City on November 15, 16, and 17, 1961. The purpose of this announcement is to present the program of the meeting which is being sponsored by the Analytical Groups (ACS) of the New York and North Jersey Sections, four sections of the Society for Applied Spectroscopy (New York, Delaware Valley, New England, and Baltimore-Washington), and the Metropolitan Microchemical Society. The meeting will consist of a series of 3-hour symposia of invited papers of extended length by experts in a number of fields of interest to analysts. The emphasis will be on recent developments in these specialties. The exhibition will consist of 75 manufacturers of scientific apparatus and supplies.

The officers are: General Chairman—Dr. S. Gordon, Fairleigh-Dickinson University; Program Chairman—Dr. E. Rosenbaum, Drexel Institute of Technology; Exhibition Chairman—N. Gardner; Arrangements Chairman—C. Jedlicka, Lucius Pitkin Co.; Publicity Chairman—A. Mowitz, Interchemical Corp.; Secretary—A. Rekus, Baltimore Gas & Electric Co.; and Treasurer—R. J. Murphy, M & C Nuclear Division.

PROGRAM

Wednesday, November 15—9:00 A.M.

DETECTORS FOR GAS CHROMATOGRAPHY

A. R. Paterson, Allied Chemical Co., Presiding

Ionization Detectors, H. McNair, Esso Research & Development Co.

Gas Density Detector, R. A. Dinerstein, American Oil Co.

Thermal Conductivity Detection, R. Kieselbach, Dupont Co.

X-RAY SPECTROSCOPY

W. J. Campbell, U. S. Bureau of Mines, Presiding

Measurement of Thin Films by X-Ray Emission Spectrography, P. D. Zemany, General Electric Co.

Applications of X-Ray Spectrography to Clinical and Biological Research, T. Hall, Sloan-Kettering Institute

Elemental Analysis (Cu, Ag, Fe) at the Subcellular Level by Means of the Electron Microprobe, A. J. Tousimis and I. Adler, George Washington University and U. S. Geological Survey

Applications of X-Ray Spectrography to Analysis of Organic Materials with Emphasis on Petroleum Products, C. W. Dwiggins, Jr., U. S. Bureau of Mines

STORAGE AND RETRIEVAL OF INFRARED SPECTRAL DATA

E. J. Rosenbaum, Drexel Institute of Technology, Presiding

Application of ASTM-Wyandotte Punch Card System, L. E. Kuentzel, Wyandotte Chemical Corp.

Computer Storage and Retrieval of Infrared Spectral Data, L. D. Smithson, Wright-Patterson Air Force Base

Use of "Peek-A-Boo" Punch Cards in Infrared Spectroscopy, N. E. Schlichter and E. Wallace, Du Pont Co.

Wednesday, November 15—2:00 P.M.

GAS CHROMATOGRAPHY WITH HIGH MOLECULAR WEIGHT ORGANIC COMPOUNDS

E. C. Horning, National Institute of Health, Presiding

Trace Analysis by Gas Chromatography, D. A. M. Mackay, General Foods Research Center

Gas Chromatographic Separations of Steroids and Related Substances, E. C. Horning, National Heart Institute

Gas Chromatography of High Molecular Weight Polyfunctional Amines, H. M. Fales, National Heart Institute

NUCLEAR MAGNETIC RESONANCE

E. G. Brame, Du Pont Co., Presiding

Applications of Varian Integrator to High Resolution NMR, J. N. Shoolery, Varian Associates

Effect of Antisotropic Molecular Motion in Solid State on the Area of the Broad Line Spectrum, R. W. Kedzie, Du Pont Co.

Quantitative Applications of High Resolution NMR, T. Benkelman, Du Pont Co.

Accuracy and Precision in Measurement of Areas in High Resolution Spectra, T. J. Flautt, Proctor and Gamble Miami Valley Laboratories

EMISSION SPECTROSCOPY

M. Margoshes, National Bureau of Standards, Presiding

Emission Spectrographic Analysis of Semiconductor Materials, D. Andrychuk, Texas Instruments

Physico-Chemical Parameters in Flame Spectroscopy, J. H. Gibson and W. D. Cooke, Cornell University

Panel Discussion: Selection of Emmission Spectrographic Equipment

Panelists: A. J. Mitteldorf, Spex Industries
R. F. Jarrell, Jarrell-Ash Co.
J. T. Rosza, National Spectrographic Laboratories
P. W. Flynn, Baird-Atomic
H. Dryer, Applied Research Laboratories

Wednesday, November 15—5:30 P.M.

SOCIAL HOUR

Thursday, November 16—9:00 A.M.

MASS SPECTROSCOPY

R. A. Brown, Esso Research and Engineering Co., Presiding

Mass Spectra of Organic Molecules (Alkyl Phenyl Sulfones), S. Meyerson, American Oil Co.

Application of High Resolution Mass Spectrometry to Organic Analysis, P. J. Klaas, Esso Research and Engineering Co.

Analysis of Solids with the Mass Spectrometer, W. M. Hickam, Westinghouse Central Laboratories

ELECTROANALYTICAL METHODS

The Scope, Application and Future of Some Newer Electroanalytical Techniques

L. Meites, Polytechnic Institute of Brooklyn, Presiding

The Past, Present and Future of High Frequency Conductance Measurements, W. H. McCurdy, Jr., University of Delaware

The Application of Unusual Electrodes to Analytical Polarography, W. D. Cooke, Cornell University

Analytical Applications of the Hanging Mercury Drop Electrodes, I. Shain, University of Wisconsin

(Continued on page 15A)

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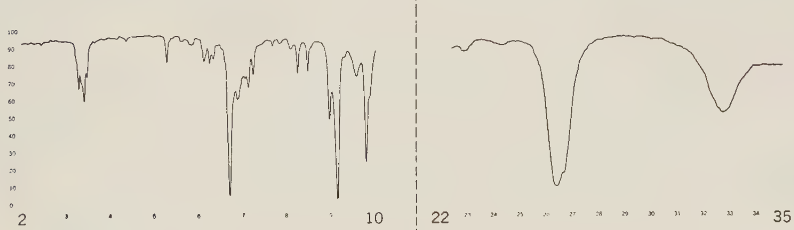

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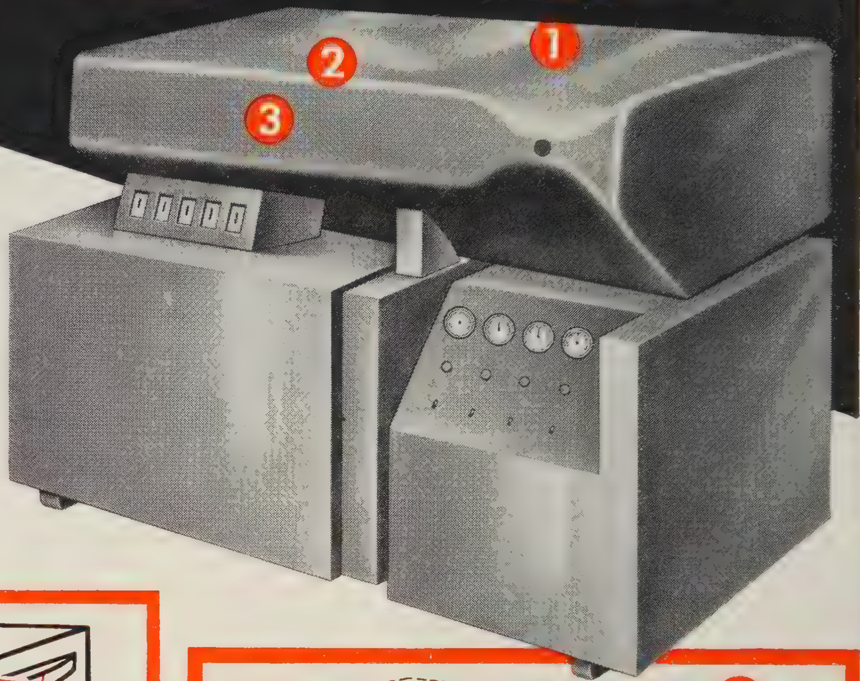

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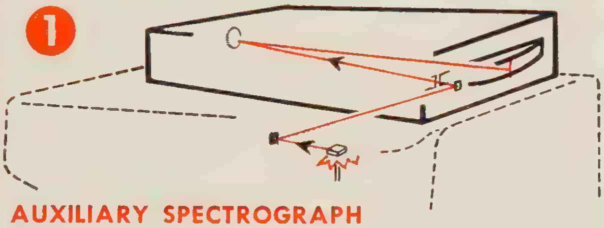
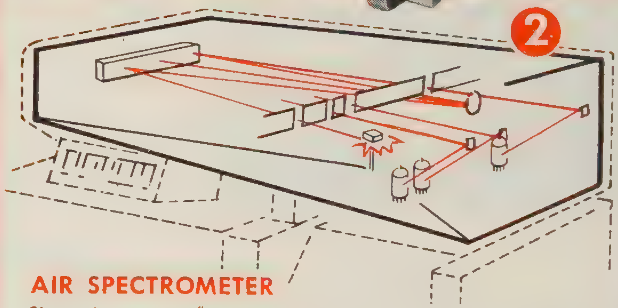


AUXILIARY SPECTROGRAPH

Mounts on top of Air Spectrometer. Range 2200A-4700A in Order I with 5.5A/mm dispersion. Provision for higher order work when used separately.



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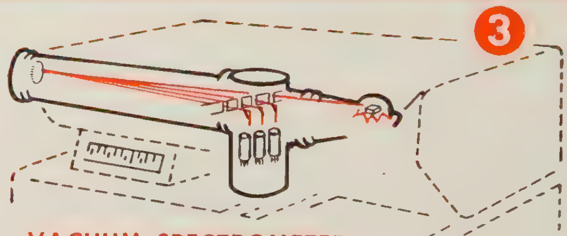


VACUUM SPECTROMETER

Mounts in front of Air Spectrometer. For C, S, P and up to five other elements. May be used in conjunction with Air Spectrometer or independently. When used in combination with Air Spectrometer, vacuum analysis of certain elements may be made without evacuating the entire unit. Typical wave length range 1750A-2600A in Order I, 5.5-A/mm with 30,000 lines/inch grating.

RESEARCH and CONTROL INSTRUMENTS, Inc.

10 JEFFERSON AVE., WOBURN, MASS.

(Continued from page 156)

AUTOMATION IN MICROCHEMICAL ANALYSIS
Panel Discussion
H. J. Francis, Pennsalt Chemical Corp., Presiding

Panelists: L. Dorfman, Ciba
G. M. Gustin, Norwich Pharmaceutical Co.
A. Steyermark, Hoffman La Roche Inc.

Complete Automation of the Microdetermination of C and N in Organic Compounds, W. Simon, Swiss Federal Institute of Technology

Advances in Instrumentation:
INFRARED SPECTROSCOPY CLINIC
J. Overend, University of Minnesota, Presiding

Thursday, November 16—2:00 P.M.

ADVANCES IN BIOCHEMICAL ANALYSIS
L. Meites, Polytechnic Institute of Brooklyn, Presiding

Electrochromatography, H. Peeters, Simon Stevin Institute for Scientific Research, Bruges, Belgium

Dye Partition Analysis, H. Goldenberg, Hillside Hospital

X-Ray Spectrometry in Analytical Biochemistry, S. Natelson, Roosevelt Hospital

Robot Chemist, A. G. Ware, Los Angeles County General Hospital

ELECTROANALYTICAL METHODS
The Scope, Application and Future of Some Newer Electroanalytical Techniques
L. Meites, Polythechnic Institute of Brooklyn, Presiding

New Methods of Titration End-Point Determination, R. B. Hanselman, Union Carbide Plastics Co.

Coulometric Titrations, A. M. Hartley, University of Illinois

Open Discussion

NEW DEVELOPMENTS IN INSTRUMENTAL TECHNIQUES FOR MOLECULAR WEIGHT DETERMINATIONS
S. Z. Lewin, New York University, Presiding

The Thermometric Method of Molecular Weight Determinations, T. Higuchi, University of Wisconsin (Tentative)

A Critical Appraisal of Instruments for Thermoelectric Determination of Molecular Weights, H. C. Ehrmentraut, Micro-Lab, Inc.

New Instrumental Approaches to Osmometry, J. E. Abele, Advanced Instruments, Inc.

The Sensitivity and Accuracy of Instrumental Determinations of Molecular Weight, S. Z. Lewin, New York University

Advances in Instrumentation:
a) EMISSION SPECTROSCOPY CLINIC
R. Bell, Lucius Pitkin Co., Presiding
b) X-RAY SPECTROSCOPY CLINIC
. Hansen, Esso Research and Engineering Co., Presiding

Thursday, November 16—5:30 P.M.
SOCIAL HOUR

Friday, November 17—9:00 A.M.
FOOD ADDITIVE ANALYSIS
M. W. Weiss, Interchemical Corp., Presiding

Separation Techniques in Residue Analysis, L. D. Metcalfe, Armour Industrial Chemical Co.

Gas Chromatography in Food Additive Problems, M. Bergick and E. M. Cohen, Evans Research and Development Corp.

Application of Analytical Chemistry to Food Additive Problems, R. T. Hall, Hercules Research Center

APPLICATIONS OF RADIOISOTOPES
G. D. Chase, Philadelphia College of Pharmacy & Science, Presiding

The Use of Radiation Sources in Analytical Chemistry, J. N. Bierly, Franklin Institute Research Laboratory

Radioisotopes—A Powerful Tool for the Analyst, D. Bandel, Tracerlab Inc.

Isotope Dilution Analysis Applied to Organic Chemistry, J. D. Moyer, W. R. Grace and Co.

ADVANCES IN PHYSICAL AND CHEMICAL SEPARATIONS
G. H. Morrison, Cornell University, Presiding

New Developments in Solvent Extraction Methods, H. Freiser, University of Arizona; G. H. Morrison, Cornell University

New Organic Reagents, F. Welcher, University of Indiana

Seldom-Discussed Organic Separation Techniques, S. Siggia, Olin Matheson Chemical Corp.

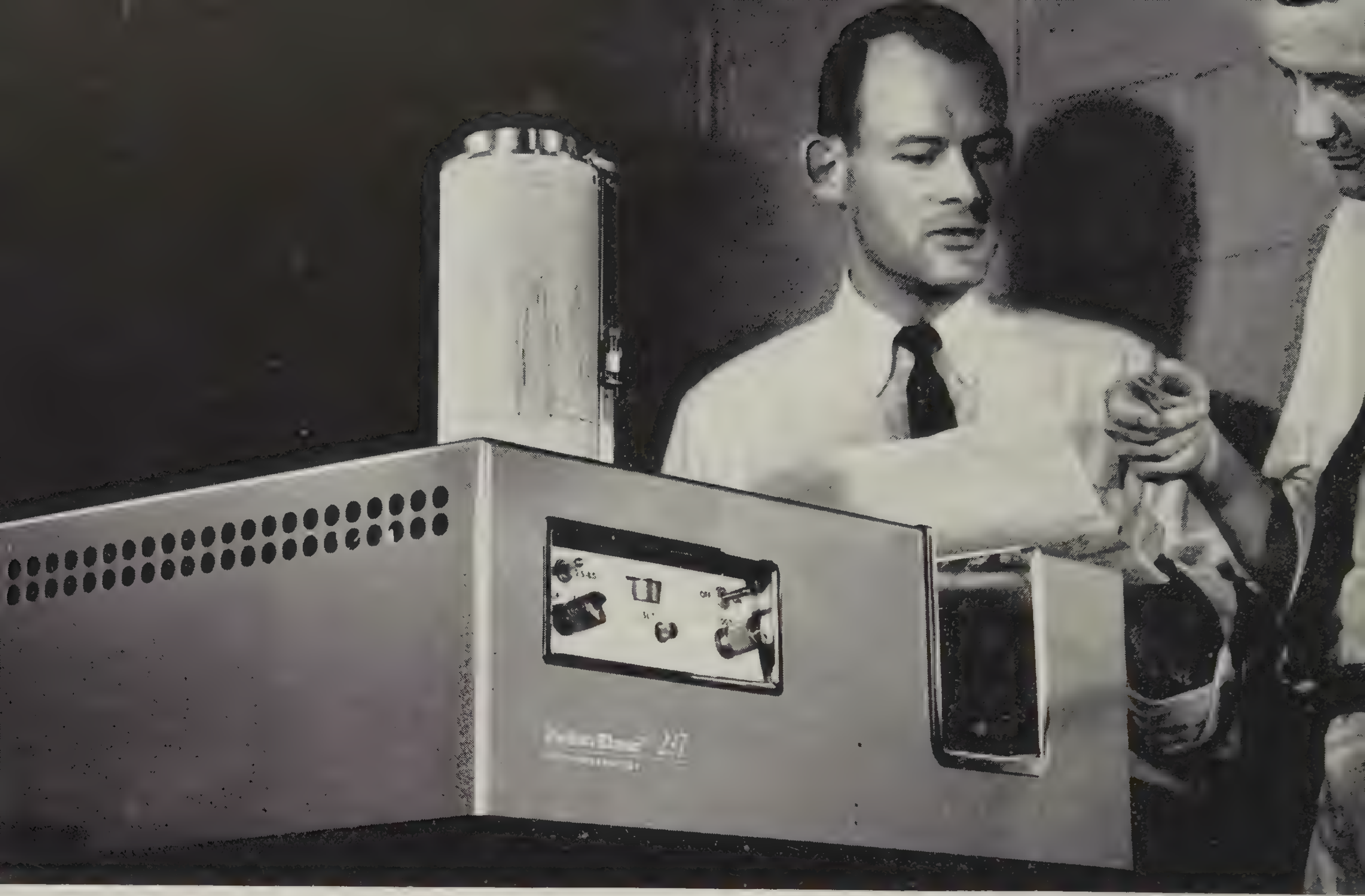
Friday, November 17—2:00 P.M.
APPLICATIONS OF NUCLEAR ACTIVATION ANALYSIS
Jane C. Sheridan, Evans Research & Development Corp., Presiding

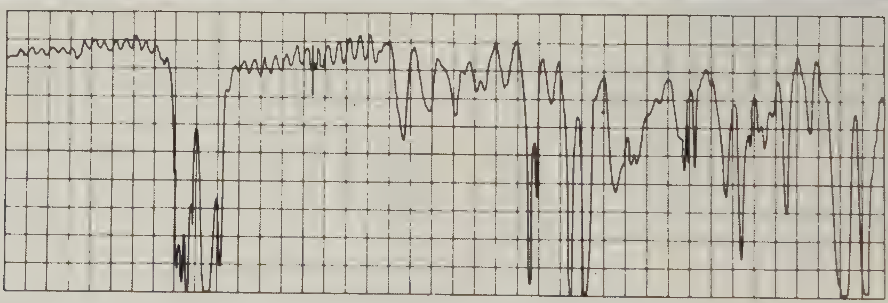
Radioactivation Analysis: Present Status and Development Trends, G. W. Leddicote, Oak Ridge National Laboratory

Application of Activation Analysis Techniques to Problems of Geochemical Interest, G. W. Reed, Jr., Enrico Fermi Institute for Nuclear Studies, University of Chicago

Criteria for Evaluating Instrumental Techniques—The Measure of Activation Analysis, D. L. Fry, General Motors Technical Center

(Continued on page 19A)





Polystyrene spectrum using an auxiliary recorder.

NOW...GRATING RESOLUTION OVER FUNDAMENTAL IR RANGE WITH NEW MODEL 237 SPECTROPHOTOMETER

You now can have the advantages of high-resolution analysis over the entire infrared spectral range of fundamental analytical importance—4000 to 625 wavenumbers (2.5 to 16 microns)...even if your budget is limited. The new Perkin-Elmer Model 237 Double-Grating Spectrophotometer, latest in P-E's low-cost Infracord line, makes this possible.

Basic to this high performance at low cost is the Model 237's grating-filter design: the dispersing power of gratings, used only in their first orders, is complemented by filters to eliminate higher orders of radiation. The result is outstanding spectral purity achieved with simplicity and dependability of mechanical operation previously not available.

Flexible Presentation. You can specify a Model 237 recording in either linear wavelength *or* linear wavenumbers, as you prefer. Full wavelength coverage is divided into two ranges—4000-1300 and 2000-625 wavenumbers; *or* 2.5-7.7 and 5.0-16 microns. The analyst selects the range he desires by the flick of a panel switch, thus assuring maximum legibility of fine structural detail.

Two scanning rates for each range are available: *fast* (8 minutes) rate for survey scans or spectra of materials with relatively few narrow spectral bands. *Slow* (24 minutes) rate provides details of very complex spectra. Here, too, a panel switch puts both speeds at the analyst's fingertips.

Optional auxiliary recorders, used above to show polystyrene spectrum, are available to give you continuous spectra at fixed wavelengths or to let you expand or compress ordinate or abscissa. The chart ordinate—a full 15 centimeters—provides maximum accuracy in recording band intensities.

Write for complete information and sample spectra.

INSTRUMENT DIVISION
Perkin-Elmer *Corporation*
NORWALK, CONNECTICUT

(Continued from page 15A)

ADVANCES IN PHYSICAL AND CHEMICAL SEPARATIONS

G. H. Morrison, Cornell University, Presiding

Resolution of Mixtures of High-Molecular Weight Materials by Use of the Microfractor, G. W. Kinzer, F. Bennington, Battelle Memorial Institute

Impurity Separation by Zone Melting: Principles and Practice, F. Moser, Eastman Kodak Co.

Resolution and Efficiency in Gas Chromatography, S. Dal Nogare, Du Pont Co.

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Mid-American Spectroscopy Symposium

Conrad Hilton Hotel, Chicago, Ill. Apr. 30-May 3, 1962

The 13th Annual Mid-American Spectroscopy Symposium, sponsored by the Chicago Section of the Society for Applied Spectroscopy in cooperation with the Cleveland, Detroit, Indianapolis, and St. Louis Sections, has been scheduled for April 30 through May 3, 1962, at the Conrad Hilton Hotel in Chicago.

Original papers on the most recent advances in Infrared, Raman, Optical emission, X-Ray, General Absorption, NMR, EPR, and Atomic Absorption will be presented. For the first time, according to Doctors John R. Ferraro and Joseph Ziomek, Symposium Coordinators, new sessions on Vacuum Ultraviolet, Gas Chromatographic Preparation of Samples for Spectroscopic Analysis and NMR Workshop—all of special appeal to spectroscopists—will be introduced at this meeting. The popular Introductory Clinic in Infrared Spectroscopy will be continued at the Mid-American Symposium. Problem clinics, seminars, and an exhibit featuring the very latest instruments and equipment will be of special interest.

For further information, write to Dr. John R. Ferraro, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois.

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Baltimore-Washington Section

Date: November 7, 1961
Dinner: Roma Restaurant, Washington, D. C. at 6:30 p.m.
Speaker: Mr. Harry Keegan, National Bureau of Standards
Topic: Spectral Reflectance
Place: National Bureau of Standards, Washington, D. C.

Date: December 5, 1961
Place: New Rolling Inn, Baltimore, Md.
Speaker: To Be Announced
Topic: To Be Announced
Time: Dinner at 6:30 p.m. and Meeting at 8:30 p.m.

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Intermountain Section

The Intermountain Section, Society for Applied Spectroscopy will conduct a symposium, particularly for spectroscopists in the Northwest to be held in Idaho Falls, Idaho on February 16 and 17, 1962. Papers on emission, absorption, X-ray, and mass spectroscopy are invited. Please submit titles and brief abstracts before December 15, 1961. For further information contact the Symposium Chairman: Mr. G. V. Wheeler, Phillips Petroleum Company, P.O. Box 2067, Idaho Falls, Idaho.

Cincinnati Section

Richard D. Ohlinger has been elected President for 1961-62. He was certified as a Medical Technologist in the Air Force in 1954 and received a B.S. from the Eastern Michigan University at Ypsilanti, Mich. in 1955. His present position is as Technologist in the Analytical Department of the National Lead Co. of Ohio and his major field of interest is mass spectrometry.

Other officers elected included: Program Chairman, Richard E. Kupel, Occupational Health Research and Training Facility, U. S. Public Health Service, Cincinnati; Secretary-Treasurer, Stuart H. Milliman, General Electric Co., Evendale; and Councilors, Norton Gerber, Formica Corp., Cincinnati, and Philip E. Berghausen, Cincinnati Milling Machine Co., Cincinnati.

Date: November 14, 1961
Meeting Place: Eagle Restaurant, Wilmington, Del.
Speaker: Dr. Abraham Savitszky, Perkin-Elmer Corp.

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Delaware Valley Section

Date: October 17, 1961
Meeting Place: Towne House, Media, Pa.
Speaker: Dr. John Margrave, University of Wisconsin
Topic: Application of Mass Spectra to High Temperature Chemistry